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High Strength Solution-Strengthened Ferritic Ductile Cast Iron

Master's Thesis
Espoo, August 10, 2015

Supervisor: Professor. Juhani Orkas
Advisor: Kalle Jalava, M.Sc

“We do not grow absolutely, chronologically. We grow sometimes in one dimension, and not in another; unevenly. We grow partially. We are relative. We are mature in one realm, childish in another. The past, present, and future mingle and pull us backward, forward, or fix us in the present. We are made up of layers, cells, constellations.”

— *Anaïs Nin*

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Abstract of master's thesis

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Abstract: High Silicon ductile iron (SSFs) represents a state-of-art in standardized ductile Iron grades, because it uniquely combines uniform hardness, intermediate strength and ductility rivalling that of some steels. Also backed by economic and technical potentials, it is imperative to take advantage of these unique properties to explore avenues to reach even higher strength levels in this grade.

Within the SSF grade, strengthening limit with Silicon is reached at 4.3wt% with mechanical properties markedly plunging at this point, necessitating the need to investigate alternative strengthening measures aside expensive heat treatments, hence thesis objective to research methods to develop high strength SSF ductile irons as-cast. Casting process and production methods to mitigate against challenges of current SSF irons also form part of this objective.

Researching and developing high strength SSF offers to the engineering materials pool, aside from obvious financial benefits, additional options in material selection for different applications, energy savings due to lighter castings, improved tool life from uniform hardness and boost knowledge on suitability of cast irons as viable replacements for steel in some applications.

The solution approach in the thesis started with extensive literature reviews and background researches on DI standardized grades with emphasis on the SSFs and strengthening mechanisms to understand present challenges of these grades. The idea was then to aim for higher strength using the EN-GJS-600-10, the SSSF grade with the highest Silicon content and strength as both reference and base iron for designing the experimental high strength SSF. Using a succession of elimination methods in the product development process based on identified parameters for high strength in DIs, such as improving graphite properties, reducing carbidic presence etc., controlled chemical composition with Cobalt (Co) as alloying element was proposed.

The result of the casting trials proved that Co indeed fortified the experimental SSF showing increase in strength and elongation. Graphite properties were improved, with refined nodules and higher nodule counts. In addition, no apparent graphite degeneracy was noticed in the microstructure with a homogenous ferritic matrix. The overall qualities of the Co-alloyed irons were better compared to the reference EN-GJS-600-10.

The significance of the results is that silicon limit in current SSF grade does not affect the possibility of reaching higher strength via controlled alloying with other element. Co alloying provided better graphite attributes in the Iron which influenced elongation and cast quality. Although from the result data, it is statistically insufficient to ascertain if further increase in Co will be proportional to strength or elongation, Co however, similar in effect to Si, stabilizes austenite contributing positively to strength, increased nucleation and nodularisation efficiency.

Keywords Ductile irons, Solution strengthened ferritic irons, solid solution, strengthening mechanisms, casting, tensile testing, microscopy

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Rilwan Okunnu

Espoo 10.8.15

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Abbreviations and Acronyms

DI	*Ductile iron*
α - iron	*Alpha iron*
δ – iron	*Gamma Iron*
SGI	*Spheroidal graphite iron*
SSF	*Solution strengthened ferritic DI*
WBS	*Work breakdown structure*
Hi-Si	*High silicon*
Fe-C	*Iron-Carbon*
C	*Carbon*
P	*Phosphorus*
Gn	*Nodular graphite*
Gf	*Flaky graphite*
Mg	*Magnesium*
Ce	*Cerium*
Fe_3C	*Cementite, also known iron-carbide*
BCC	*Body centered cubic*
FCC	*Face centered cubic*
HCP	*Hexagonal close packed*
CHG	*Chunky graphite*
CE	*Carbon equivalent*
RE	*Rare earth*
Pb	*Lead*
Sb	*Antimony*
O	*Oxygen*
S	*Sulphur*
Al	*Aluminum*
Cu	*Copper*
Zn	*Zinc*
Cr	*Chromium*
Sn	*Tin*
B	*Boron*
Bi	*Bismuth*

Introduction

Constantly evolving trends and increasing functional requirements of mechanical products and structural designs has placed quite a premium on engineering materials. Coupled with sustainable energy and environmental considerations, lightweight designs are central to improving efficiency and optimize energy consumption. It is imperative that enhanced materials are continuously researched and developed to meet these demands. Finding these solutions at relatively low cost and short lead time are essential parts of the development process for such engineering materials whilst not compromising on their structural integrity and mechanical properties.

Casting as a manufacturing process offers promising options in this area with development of new cast Iron grades driving the surge. Within the available cast irons grades offering attractive combination of excellent mechanical properties, castability and low cost, spheroidal graphite cast irons (SGI) have been thrust into the serious discourse as comparable alternatives to steels in numerous engineering applications. More prominently, the grades specified in the EN 1563:2012 standard- the first and second generations of ductile Irons (DI). These are also known as the ferritic-perlitic and solution strengthened ferritic (SSF) ductile iron also sometimes referred to as high-silicon (Hi-Si) irons[1]. These two DI grades are particularly important amongst the different classes of cast irons because of their castability in complex geometries, excellent mechanical properties and relative low cost.

In the ferritic-perlitic DI grade, some challenges like hardness variation caused by a composite matrix of ferrite and perlite creates machining difficulties and limited elongation thus making its use restricted to specific applications where these features are not specifically demanded. Conversely, the development of the SSF grades has however provided a solution to this problem and this has furthered the positive reception and huge market penetration it has been getting with increasing usage in different engineering applications. Nonetheless, it is still necessary to consolidate on this momentum by understanding, researching and developing methods to improve mechanical properties and technical appeal of this grade relative to current market and material requirements. This essentially means pushing the limits on current properties of the SSF irons even further through the development of iron grades with higher strength and/or elongation without adverse economic or production disadvantage. The current SSF grades therefore presents a good start point to evaluate for further possibilities in fortification for high strength SSF irons.

Current limitations in properties achievable with current SSF grades is the alloying amount allowed in the solid solution with silicon. It is known that the matrix governs much of the mechanical properties of iron castings and the matrix itself is influenced with the casting production paths: solidification (as-cast) and heat treatment (post production). For obvious reasons, solidification provides a more economically feasible route to achieve the desired microstructure using sound composition control of alloying elements compared to expensive heat treatment and time consuming secondary post-production activities. Against this logic, the thesis focuses on solidification to achieve high strength as-cast for the intended SSF iron. Additional benefit of using this method is that as-cast characteristics of DI are based on calculated composition which is representative of alloying constituent. Therefore, this thesis work explores the possibilities within this production route and aims to fill the knowledge gap within this perspective for high strength DI.

1.1 Purpose

SSF irons represent a state of art in current grades of standardized DIs with superior mechanical properties based on a predominantly ferrite matrix. These excellent properties however drastically deteriorate at over 4.3wt% silicon addition[2,3] in solid solution strengthening implying inability to reach higher strength by this alloy or method alone. This objective of this thesis is therefore to find potential means of reaching higher strength in SSF iron as-cast and in doing so explore suitable strengthening alternatives to heat treatment for this. In addition to evaluating causes and effect of the sudden drop in properties at over 4.3wt% silicon content, understanding how current SSF grades differ from earlier standardized grades in terms of microstructural composition and effects of composition on the microstructure is also included in the work-breakdown structure (WBS) for the thesis goal. These two aspects of the WBS were included in the solution scheme as necessary requisite to understanding and assessing whether solution strengthening with Silicon alone is no longer sufficient to reach greater strength value. Clear appraisal of this fact in relation to current SSF grades will provide a useful incentive to evaluate new possibilities for further strengthening as well as with other alloying alternatives. In summary, while not restraining possibilities in potential outcome of the thesis, a good target still for high strength SSF would be an experimental iron with properties besting the EN-GJS-500-14 or EN-GJS-600-10 as-cast in either tensile strength and/or elongation.

1.2 Approach

Addressing the problem statement of the thesis requires a systematic approach to solution plus extensive research and literature review covering existing studies on standardized DI grades. The work breakdown structure and solution formula for the thesis problem starts with a detailed theoretical background familiarizing with development concepts behind standardized grades with particular emphasis on the ferritic-perlitic and SSF grades followed by methods in strengthening mechanisms. The WBS is then detailed down to the literature review utilizing a thematic approach to examine researches covering the SSF grades and factors affecting their mechanical properties. More focus here would be on challenges of the SSF irons, studying and discerning different viewpoints from researches, role of constituent alloys on microstructure, limiting effects of solution strengthening with Si, and inferences on potentials for reaching high strength. The results of which would be synthesized to propose alternate potential composition which would be experimentally developed and characterized from standardized test. The solution approach for the WBS is summarily broken down in this order.

1. Review of existing literatures covering standardized grades specifically focusing on the ferritic-perlitic and SSF grades. Assessing present challenges and effects of composition on microstructure and mechanical properties of these grades.

2. Based on insights from the previous step, inferences on material parameters supporting high strength based on material properties' indicators would be synthesized to form the governing criteria for a decision matrix matched with an appropriate strengthening method suitable to produce high strength SSF as-cast.

3. The outcome of studies into feasible strengthening method compared against parameters supporting high strength will lead to a proposed composition for high strength experimental iron. Composition control of elements based on the collective and individual activity is an important highlight of this step.

4. Development of experimental iron from casting trials and characterization of the iron through microstructural and mechanical properties analysis.

5. Result analysis and discussion of outcomes comparing experimental iron to a reference SSF grade for validation of properties as specified for standardized SSF.

1.3 Delimitation

It is necessary to mention that considering the scope and timeframe for completing this thesis work, some aspects of work related to this topic would not be covered. Some of these areas while pertinent to the thesis subject would require more time and wider technical resources to cover hence their delimitation. The casting trials and mechanical testing would only cover static mechanical properties. Cyclic or dynamic mechanical properties are not included in the tests because primary properties essential to the required iron characterization are adequately satisfied by static properties analysis alone. Likewise, metallurgical characterization will not include crystallographic evaluation or mechanical behavior of the test casts. These aspects would require extensive studies done in another field of study, related to material physics. Areas such as these not covered in this work would nonetheless be recommended in the final section of the report as recommendation for future research work.

2 Theoretical background

2.1 Cast Irons

Cast irons are engineering materials from the ferrous metal taxonomy developed in 1948 with carbon contents above 2.14wt%[4]. In practice, cast irons actually contain 3-4.5wt% carbon and depending on application, the inclusion of other relevant alloying elements notably silicon. The carbon concentration minimizes the melting temperature from the eutectic point 1150ºC - 1300ºC which is significantly lower than that of steel and with this fluidity, making castability relatively easy. Addition of other alloying element in cast irons production may however affect the maximum solubility of carbon in austenite in which case eutectic structures with less than 2 wt% carbon can be attained in such alloys[4,5] . The microstructure of cast irons are formed and largely dependent on chemical composition which in turn determines mechanical properties and general characteristics of the cast iron.

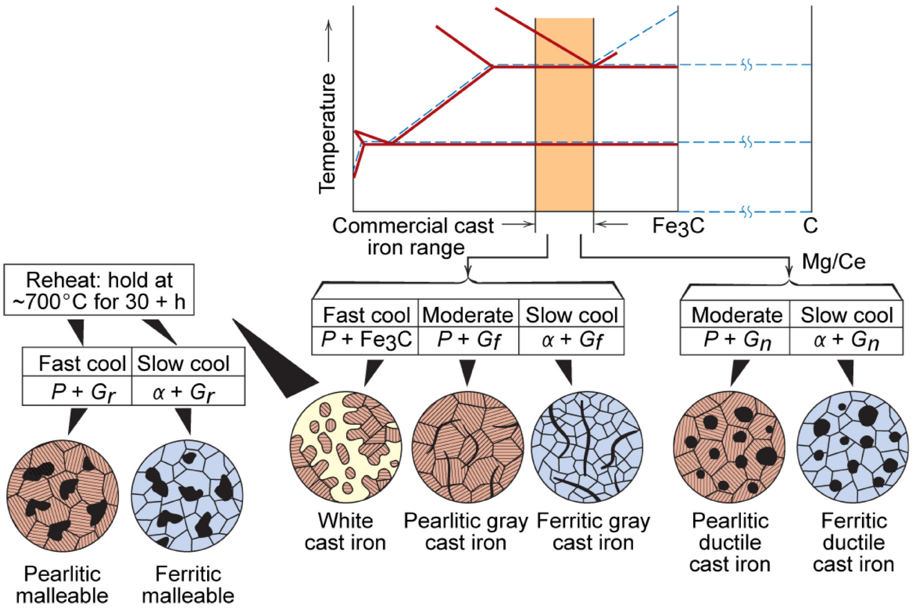


Figure 2-1. Classification of cast irons - Cooling rates and microstructures[4].

Cast irons exist in four common classifications based on metallurgical characteristics as illustrated in figure 2.1. The classification above categorizes cast irons in terms of solidification and microstructure. Gray cast irons are characterized by flaky graphites in either perlitic or ferritic matrix, ductile or nodular iron through the addition of magnesium, cerium or yttrium in a process known as "nodularisation" produces ductile iron with spheroidal or nodular graphite similarly in either perlitic or ferritic matrix. The flaky graphite in gray cast irons acts as stress concentrators making it extremely susceptible to brittle failure compared to the spherical graphite in ductile Irons. The other types of cast irons are white irons which are even more brittle because of carbon existing mostly as cementite in its microstructure[4,6]. Malleable cast irons are the heat-treated variation of white irons while the last types are vermicular or compacted-graphite irons which combine microstructural properties of both gray and ductile irons with a worm-like or vermicular shaped graphite.

Production of cast irons

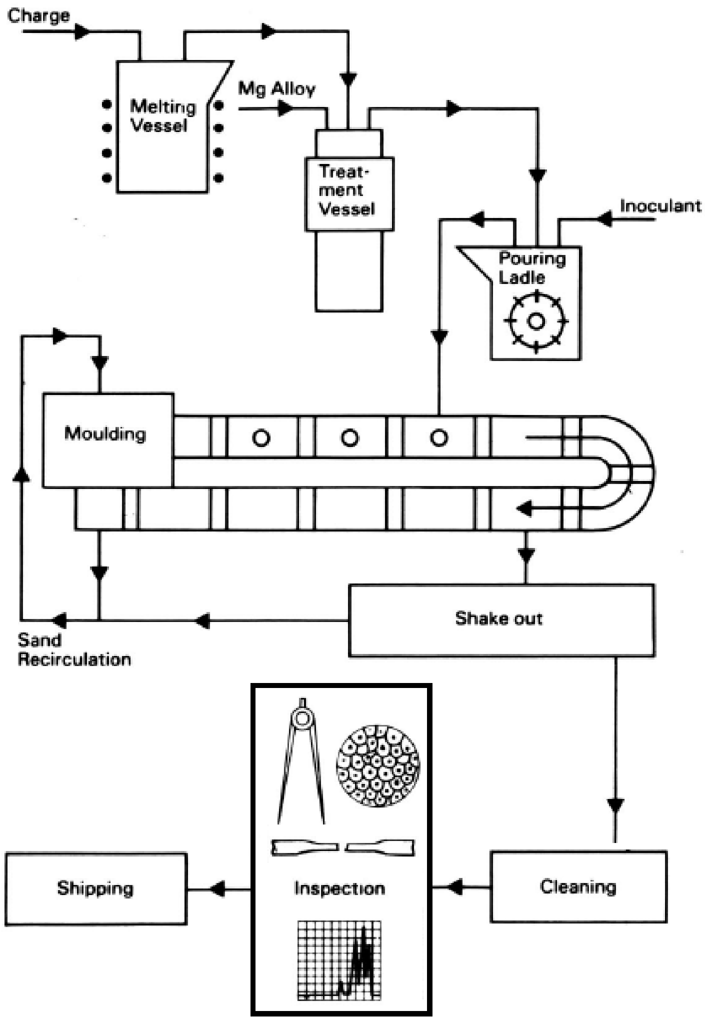


Figure 2.2

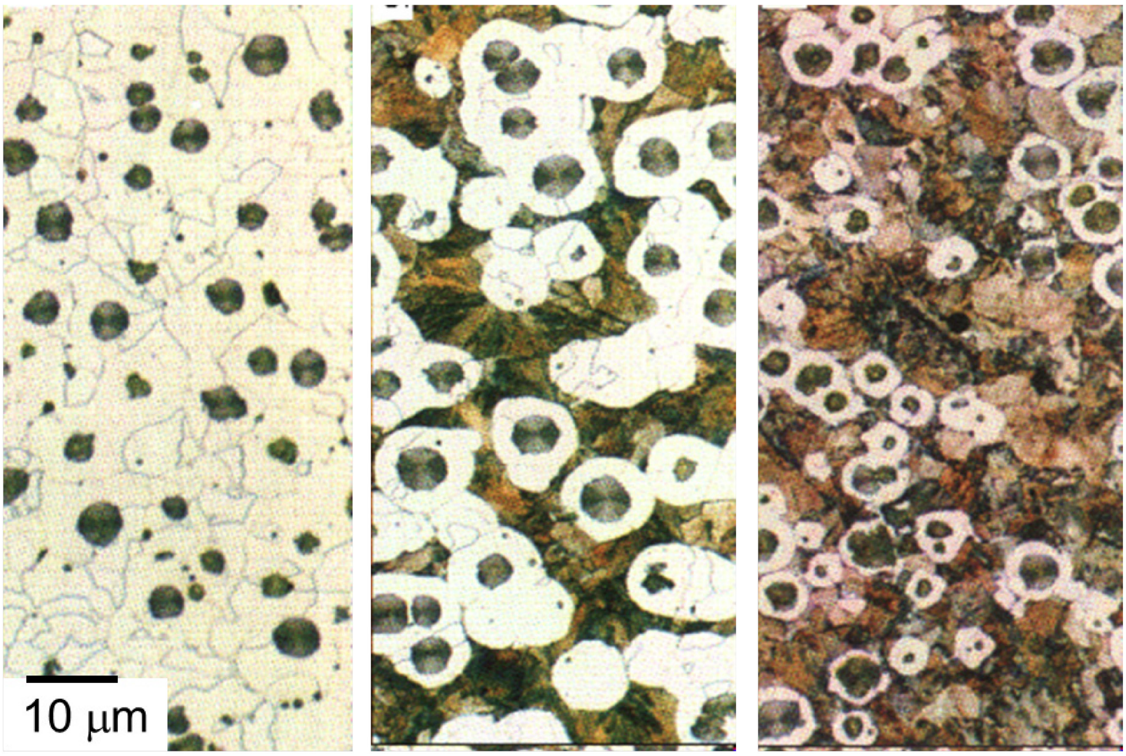
Figure 2-2: Typical commercial production process of ductile irons[5]

The production route in the figure 2.2 above shows the different stages involved in production of ductile irons in the foundry. With the exception of inoculation and addition of Mg Alloy for nodularisation, the process is similar for other cast irons too. The charge in theory represents the chemical composition of the cast irons which include main elements like carbon, silicon and phosphorus.

2.2 Ductile Irons

Ductile irons (DI), also referred to as nodular or spheroidal graphite irons (SGI) are produced through the addition of either cerium, yttrium or magnesium in the liquid cast iron melt to precipitate the graphite as spheroids or nodules. As exemplified in the classification method used in figure 2.1, solidification sequence and composition control of alloying elements in the chemical composition determines the microstructure of DI resulting in a wide range of grades available today. As the name implies, ductile irons have significantly higher tensile elongation and substantial strength compared to gray irons for example, primarily because of the graphite morphology. The spheroidal graphites act as dislocation inhibitors because of its surface area to volume ratio compared to flaky graphites in gray irons which act as notches or stress concentrators. For DI, the microstructure comprise micro constituents describing nodule count, matrix structure and "nodularity" which have significant influence on properties of the iron individually or in combination[6,7]. The guidelines on nodularity for DI are designated in the EN-ISO 945-1 dividing nodule forms into categories I to VI, form V and VI being the most optimal. The nodularity is integral to mechanical properties such as toughness and elongation and there is often a strong correlation between deterioration of properties and deviation of the nodules from the recommendable forms V, VI. High nodule count is also very desirable to some mechanical properties and it is one of the benefits of effective inoculation in DI production.

Inoculation is an important aspect of cast iron production and performed to provide sufficient nucleation sites for dissolved carbon to precipitate as graphite rather than cementite Fe_3C in the iron. This is achieved by preventing undercooling below the metastable eutectic temperature where brittle white iron structures are formed[8]. Depending on the cast iron type or chemical reactivity of constituent alloys in the charge, the inoculants may be added in either the treatment vessel or pouring ladle as in schematic depicted in figure 2.2. Available grades of DI exist typically from fully ferritic to fully perlitic depending on the chemical composition, production method or grade. The percentage ratio of ferrite and perlite in the matrix structure typically governs the material strength. DI as-cast are commonly pearlite which is a micro-constituent comprising alternating layers of ferrite and cementite. The ferrite matrix which represent the pure phase of iron can be derived through heat treatment or appropriate alloying composition. Ferrite has low strength and hardness but relatively high toughness and ductility while perlite has high strength and hardness but low ductility. As mentioned earlier, both types of matrices can be produced as-cast in DI completely or in shared ratio through controlled heat-treatment, composition control or solidification sequence. Figure 2.3 shows the three possible DI microstructures attainable from either of the process mentioned above and as seen from all three microstructure, a common feature are the nodular graphites.



(a) (b) (c)

Figure 2-3: Typical microstructure of nodular cast iron,
(a) Fully ferritic matrix, (b) ferritic-perlitic matrix, (c) fully perlitic matrix.

The iron-carbon diagram (Fe-C phase diagram) in figure 2.4 describes the different phases of iron relative to solubility limits of carbon. This diagram best explains the solidification process of DI producing those microstructures above. The Fe-C diagram shown is only a portion of the whole diagram ending at a maximum carbon composition limit 6.7wt% with a cementite matrix. In practice, this means all steels and cast irons have lesser carbon content[4]. Pure iron can exist in three phase forms when melted as indicated on the leftmost axis. Ferrite or α-iron at room temperature up to 912°C with BCC crystal structure and maximum carbon solubility of 0.22wt%, austenite with a FCC crystal structure upon further heating up till 1394°C and as δ-iron up until 1538°C which is the melting point of iron. The δ-iron is structurally the same as α-iron, the only difference being the temperature ranges in which they exist. Phase transformation with respect to austenite is of prime importance to cast irons, it has maximum carbon solubility of 2.14wt% at 1147ºC and the FCC crystal structure permits this amount due to larger interstices for carbon in the solid solution. Austenite does not exist below the lower critical temperature- 727ºC at which point the metastable cementite Fe_3C forms.

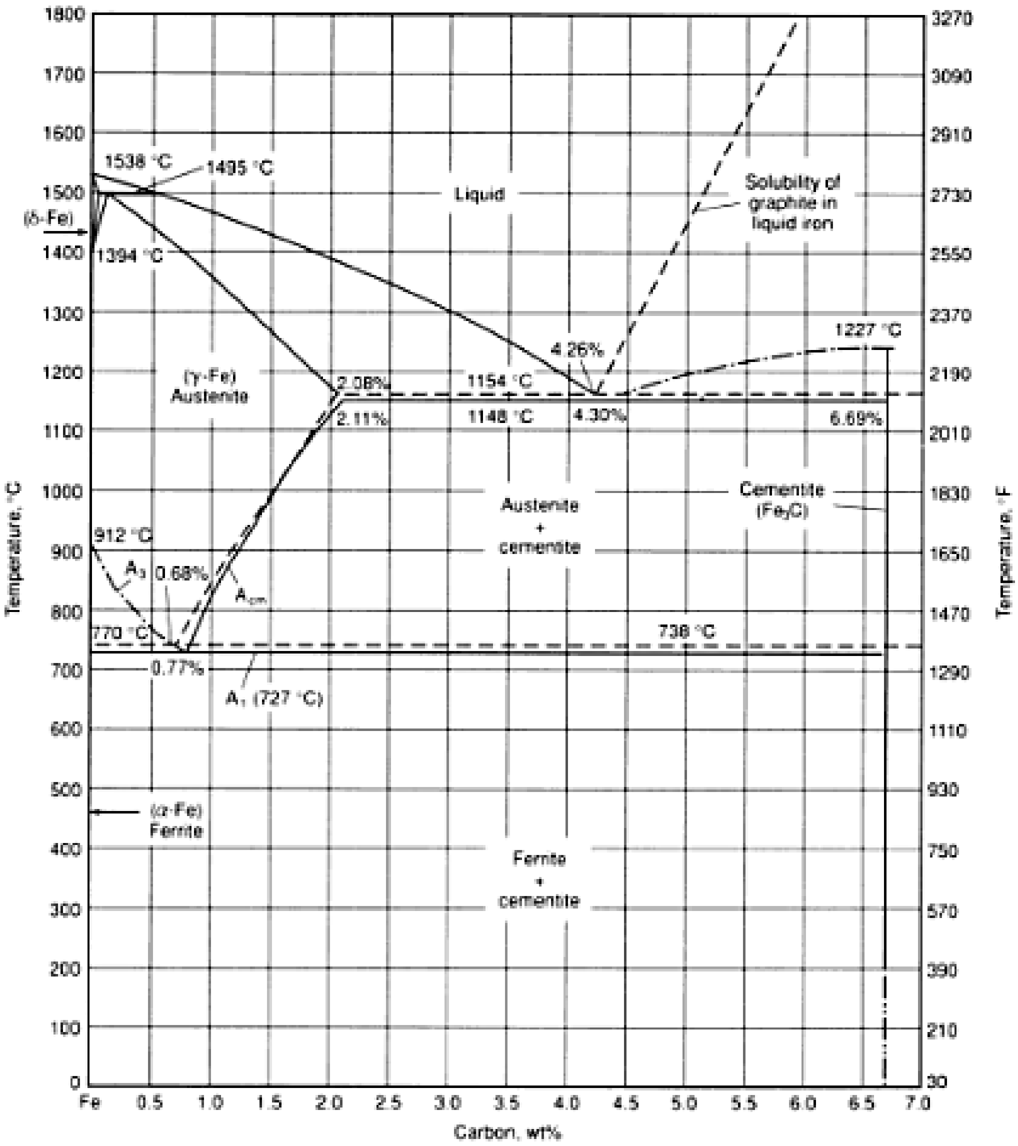


Figure 2-4. Iron-Carbon phase diagram[4]**

**Solid curve represents the metastable system Fe-Fe_3C and dashed curves represent the stable system iron-graphite

2.3 Typical Ductile Iron composition

DI are used in many applications where combined qualities of strength and ductility are essential. In contrast to gray iron for instance, strength in DI is doubled and elongation raised by factor 20[4]. These properties are attributed to primary chemical composition of DI which might of course vary depending on foundries and influenced by purity level of scrap metal used in the melt charge during castings. Typical composition of DI consist of five main element namely Carbon (C), Silicon (Si), Manganese (Mn), Phosphorus (P) and Sulphur (S), often forming the group of alloys known as the DI base composition. Inclusion of other element to the composition is dependent on client requirements, desired microstructure and probably individual foundry practices. Each of these elements in the base composition has its individual and combined benefit with other elements in the charge. Therefore based on the final composition, solidification can be thus hypoeutectic, hypereutectic or eutectic describing the carbon equivalence (CE) below, over and at 4.33 respectively. Although occasionally varying based on composition or study purpose, the most common formula for calculating carbon equivalence is

$$C.E = \%C + (\%Si + \%P)/3$$

Of the main elements, Si is an essential addition because it is a strong ferrite promoter, increases hardness, tensile and ultimate strength. It decreases chill tendencies in cast irons, carbon solubility in austenite (eutectivity), improves graphite precipitation and increase ductile-brittle transition temperature. Higher silicon content in the composition increases ferrite strength and reduces impact resistance. It also provides high temperature oxidation resistance to the cast. Beneficial Mn levels are recommended below 0.2wt% as-cast because it poses segregation risks around grain boundaries and promotes carbide and mild perlite. Mn as well as S in the composition is often a concern when choosing iron scrap for the melt and as such a serious concern for production foundries. P above 0.05wt% is similarly a segregation risk and produces carbides or phosphide complexes. It also embrittles the iron by raising the ductile to brittle temperature. The inclusion of S in DI casting is a basic necessity to make nodularisation possible but its quantity in the composition should be critically regulated because excess or inadequate quantity is detrimental to properties as it advances formation of poor and quasi-flaky graphites. Percentage addition in the range of about 0.015wt% has been commonly used and recommended in DI production. Deliberate addition of magnesium (Mg), cerium (Ce), calcium (Ca), or Yttrium (Y) [9] as spheroidizing agent is an extremely essential activity in DI production because they are responsible for precipitation of the graphite as spheroids. Ferrosilicon magnesium (Fe-Si-Mg) is widely used in castings nowadays because of its low cost and applicability to various castings with different sections and C.E values[9]. It is therefore necessary to understand and use these main elements in moderation based on individual application as misappropriation of required amounts could lead to poor properties for resulting castings.

2.4 Standardized grades - DI

The term standardized grades encompasses the different classes of DI designated in the European standard (EN standards). These DI classes comprise the so-called "first generation ductile irons" also known as the ferritic to perlitic grades, the "second generation ductile irons" or solution-strengthened ferritic (SSF) irons, both specified in the EN:1563 standard and the Austempered DI (ADI) introduced in EN 1564:1997 standards. The major distinction between these grades comes largely from their different microstructures and method of production. The ferritic to perlitic grades were developed during the second half of the 20th century and are the more commonly used DI. The matrix ratio of ferrite to perlite is determined by regulating the amount of perlite forming agents in the chemical composition, typically containing about 2-2.5wt % silicon[10]. Amongst this grade, the ferritic-perlitic grade EN-GJS-500-7 is quite popular largely because of its combined ferrite and perlite structure providing attributes of both matrixes. But inconsistencies in properties like strength, hardness distribution and low ductility are some of the challenges experienced with the ferritic to perlitic grade. Also due to sensitivity to local cooling and pearlite-stabilizing elements in its microstructure, machinability is quite demanding in this grade, resulting in lower tool life, extra costs and dimension control issues in its cast component[7]. These problems are even more apparent in castings with varying thicknesses and different batches.

The SSF iron or high-silicon irons are produced by solution strengthening of the ferrite with Si and they combine unique properties of intermediate strength and high elongation compared to equivalent grades in the ferritic to perlitic grades. The Austempered ductile irons -ADI or kymenite developed in Finland, is an isothermally heat-treated ductile iron with an ausferritic matrix. The ausferrite is a combination of acicular ferrite and carbon-stabilized austenite possessing a combination of remarkable strength, hardness, toughness, ductility and machinability. It is produced by a two-stage austempering process which starts with heating and holding the cast at its "austenisation temperature" 900^{o}C for about an hour and half to saturate the austenite with carbon after which it is then quenched rapidly and isothermally held at its "austempering temperature" 400^{o}C usually in a salt bath before allowing to cool at room temperature[9]. The table 2.1 and 2.2 lists different irons in the ferritic to perlitic and ADI grades specified in the EN 1563 and 1564 respectively.

Table 2-1. Ferritic to perlitic grades specified in the EN 1563[1]

Material designation		Tensile strength R_m N/mm^2	0,2 % proof stress $R_{p0,2}$ N/mm^2	Elongation A %
Symbol	Number	min.	min.	min.
EN-GJS-350-22-LT 1)	EN-JS1015	350	220	22
EN-GJS-350-22-RT 2)	EN-JS1014	350	220	22
EN-GJS-350-22	EN-JS1010	350	220	22
EN-GJS-400-18-LT 1)	EN-JS1025	400	240	18
EN-GJS-400-18-RT 2)	EN-JS1024	400	250	18
EN-GJS-400-18	EN-JS1020	400	250	18
EN-GJS-400-15	EN-JS1030	400	250	15
EN-GJS-450-10	EN-JS1040	450	310	10
EN-GJS-500-7	EN-JS1050	500	320	7
EN-GJS-600-3	EN-JS1060	600	370	3
EN-GJS-700-2	EN-JS1070	700	420	2
EN-GJS-800-2	EN-JS1080	800	480	2
EN-GJS-900-2	EN-JS1090	900	600	2

Table 2-2. Austempered ductile iron grades as specified in the EN 1564[1]

Material designation		Tensile strength R_m N/mm^2	0,2 % proof stress $R_{p0,2}$ N/mm^2	Elongation A %
Symbol	Number	min.	min.	min.
EN-GJS-800-8	EN-JS1100	800	500	8
EN-GJS-1000-5	EN-JS1110	1000	700	5
EN-GJS-1200-2	EN-JS1120	1200	850	2
EN-GJS-1400-1	EN-JS1130	1400	1100	1

2.5 Solution strengthened Ferritic DI - SSFs

The SSF grades also known as high silicon irons (Hi-Si) were first developed in the early 90s after extensive researches into drawbacks of the ferritic to perlitic grades. The outcome was the SSF grades with a distinct blend of intermediate strength and excellent ductility. SSF irons are produced by the solid solution strengthening of the ferrite matrix with about 3.0 - 4.4wt% silicon instead of copper (Cu), Mn, or Tin (Sn) resulting in a ferritic matrix[2,7,10]. The Si alloying rate is constant depending on SSF grade unlike other DI grades where alloying additions are dependent on casting geometry and size[2,11]. It therefore creates consistent properties in all sections of the casting and same in batches. The high Si content also suppresses the worst influence of carbide generating elements present in the cast which are often deleterious to DI properties.

In comparison to the ferritic to perlitic grades which derives its strength largely from the composite ferrite and perlite matrix, the SSF with perlite limited to 5% is strengthened by the ferrite matrix. This matrix is responsible for the uniform hardness distribution and significant improvements in machinability compared to other grades. With better elongation, almost triple that achievable on the ferritic to perlitic grades, the SSFs also offer about 13-27% increase in yield strength and less sensitivity to carbide formation. More so, lightweight castings from this grade are possible leading to about 1.5% weight reduction[11] offering energy and material savings plus better dimension control and geometric tolerance. The high silicon content furthermore increases the eutectoid temperature of casting thereby improving performance at elevated temperature. Various studies also have confirmed their better weldability and significant reduction in weight and machining costs when considered as direct replacement for steel in similar applications. Table 2.3 lists the three irons currently specified for the SSF grade in the EN 1563.

Table 2-3. SSF grades specified in the EN 1563[1]

Material designation		Relevant wall thickness	0,2 % proof strength	Tensile strength	Elongation
		t	$R_{p0,2}$	R_m	A
		mm	MPa	MPa	%
Symbol	Number		min.	min.	min.
EN-GJS-450-18C	5.3108	$t \leq 30$	350	440	16
		$30 < t \leq 60$	340	420	12
		$60 < t \leq 200$	Guidance values to be provided by the manufacturer		
EN-GJS-500-14C	5.3109	$t \leq 30$	400	480	12
		$30 < t \leq 60$	390	460	10
		$60 < t \leq 200$	Guidance values to be provided by the manufacturer		
EN-GJS-600-10C	5.3110	$t \leq 30$	450	580	8
		$30 < t \leq 60$	430	560	6
		$60 < t \leq 200$	Guidance values to be provided by the manufacturer		

2.5.1 Mechanical properties of SSFs

The distinctive feature of better elongation, yield strength and machinability are the most crucial properties that has propelled the SSFs into wider acceptance over the ferritic to perlitic grades. With respect to the many applications using the SSF castings, these properties have proved very critical thus validating its appeal as a viable option with growing prospect and utility. Figure 2.40 highlights the comparison of the standardized grades with regards to their yield to tensile strength ratio. The SSF has a ratio of approximately 85% compared to about 65% for the ferritic to perlitic grades as tested from 25mm cast samples[1,]. Despite the higher ratio, elongation values are still significantly higher than the ferritic to perlitic grade. This is because of the influence of its composition and structure impeding more dislocation movement which governs material yield strength than tensile strength. This is also evident from the plot indicating concurrent difference in fracture elongation A_5 relative to yield strength $R_{p0.2}$ between conventional grades with equivalent strength from the SSF EN-GJS-500-10 and ferritic to perlitic grade EN-GJS-500-7 in figure 2.5. The SSF obviously has the edge over the other grade in the figure too.

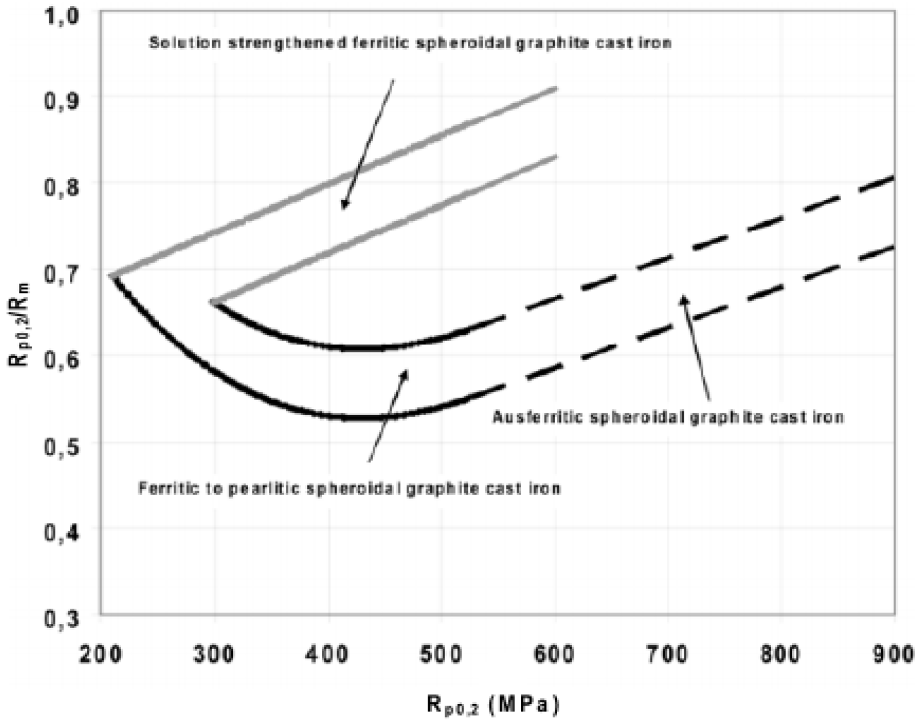


Figure 2-5: Ratio 0.2% proof strength /tensile strength[1]

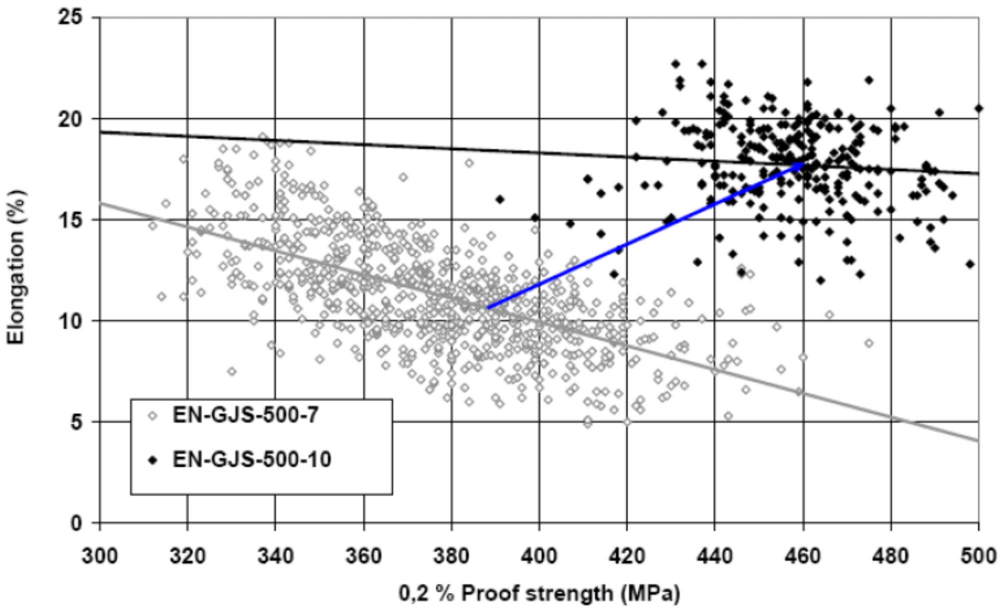


Figure 2-6 : Elongation vs 0.2% proof strength[1]

In practice and for foundries, machinability is an integral aspect of casting production, the SSFs make it less demanding to comply with hardness tolerance, dimension control and preserve tool life. Studies from different foundries have reported up to 20% reduction in machining costs with SSFs compared to ferritic to perlitic grade due to uniformly distributed hardness in SSF microstructures[11]. Figure 2.7 corroborates this claim from the tests results on machinability and machining costs investigated by examining hardness variation across different sections of a wheel hub manufactured from EN-GJS-500-7 ferritic-perlitic grade and SSF grade (EN-GJS-500-14). As seen on the images in figure 2-7, the very high peaks and troughs in the adjoining graphic illustration outlines the high disparity in hardness across the sections of the EN-GJS-500-7 wheel hub versus the tiny bumps in the outline for the hub from the EN-GJS-500-14 SSF grade. Evidently the high and low peaks signify a tedious machining operation riddled with lots of starts and stops due to the uneven hardness distribution in the metallographic structure of the ferritic-perlitic grades. This translates to enormous amount of wear on the machining tools too.

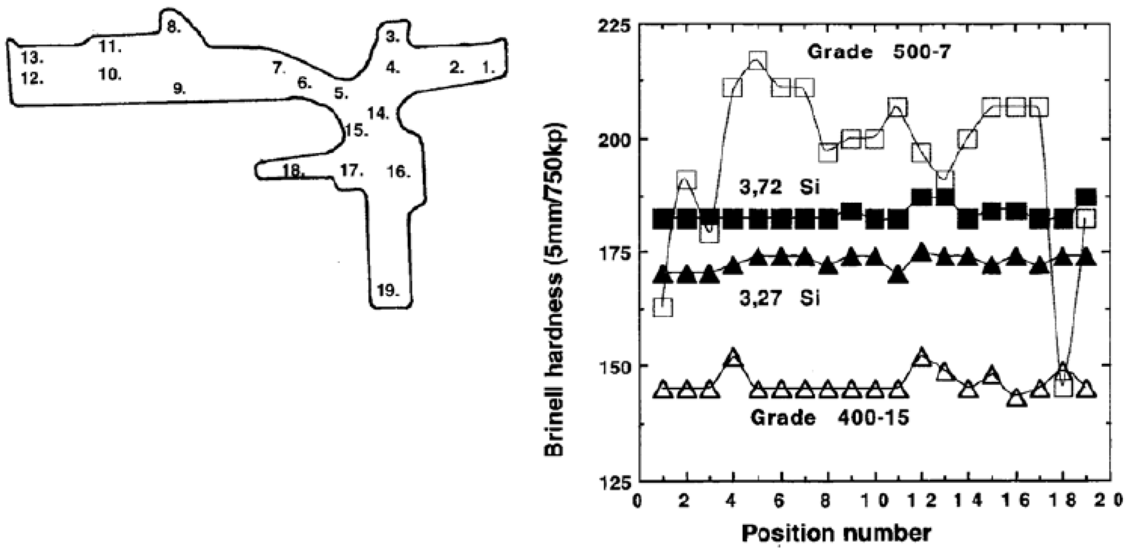


Figure 2-7. Hardness variation in ferritic-perlitic grade vs SSF grade[11]

Likewise, the surface roughness of both grades is also related to ease in machinability. From tested samples, the influence of the matrix in SSFs gives better benefits on surface roughness as seen from the type of chips generated from cutting operations involving EN-GJS-500-7 and SSF grade- EN-GJS-500-14. Using machining parameters, cutting speed (Vc) at 320m/min, depth (Vb) at 200µm, feed rate 0.15mm and tool radius (a_p) at 0.5mm, the longer and curly chips in the figure 2-8 indicative of a smoother machining operation due to lower hardness variation is for the SSF iron while the smaller and sturdy chips representative of intermittence in cuts is for the ferritic-perlitic iron.

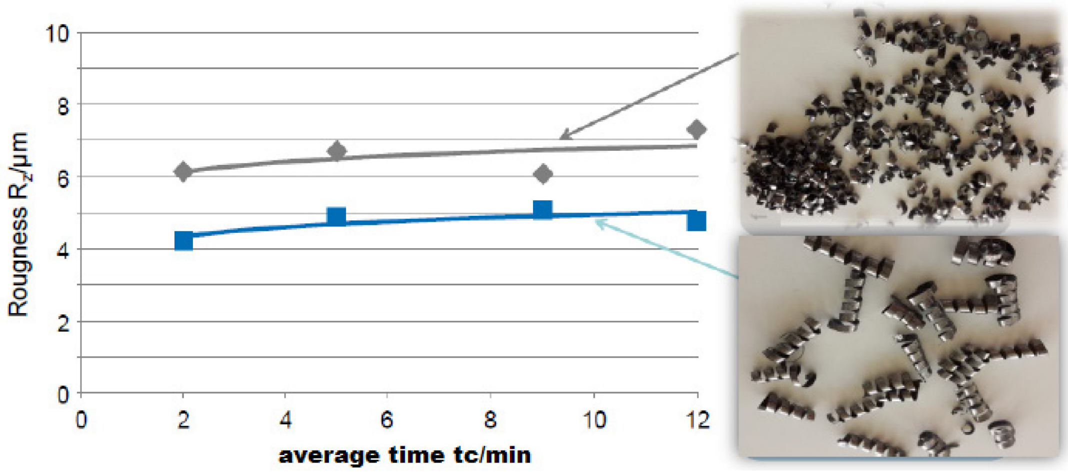


Figure 2-8. Influence of matrix on surface roughness. EN-GJS-500-7 vs EN-GJS-500-14.[11]

Additionally, yield strength in the SSF grades are higher than tensile strength and when both strength parameters are compared to hardness for SSF and ferritic to perlitic grades, the yield strength values in SSF irons are significantly higher for an equal value in hardness. The tensile strength however has more or less a proportional relationship with the hardness values for both DI grades. This is explained by the results presented on these findings in the EN 1563 standard comparing this property in both DI grades in figure 2-9. This form of material response in the SSF grade can be partly attributed to lower perlite content in the SSF matrix and the independence of hardness on other micro-constituent in the SSF microstructure.

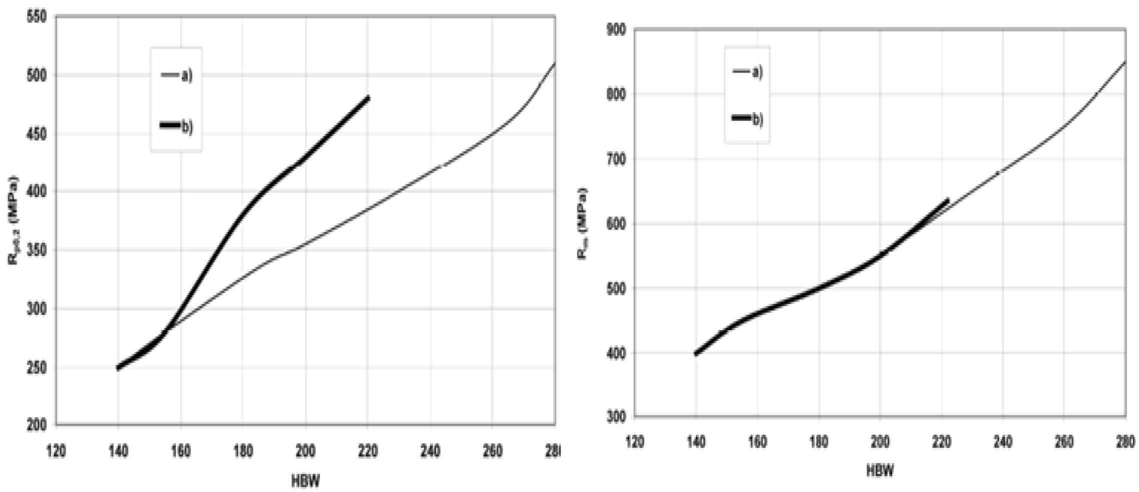


Figure 2-9 (left). Relation between Brinell hardness and 0.2% proof strength (Right) hardness and tensile strength.[1]

For other SSF material properties, impact energy and fatigue properties are comparable to the ferritic to perlitic grades due to high silicon content[3,10,12]. For impact energy, it is important to understand that standard test procedures forming conventional opinions do not entirely replicate practical realities in simulated tests which have led some researchers and even the EN standard to explain that the Charpy test although very common uses a strain rate about four orders of magnitude higher than rates experienced in even severe applications[1]. The geometry of test casting samples are often not subjected to some important loading conditions which might affect the results of such test. Also, the Charpy test is not the most suitable method for impact energy evaluation in cast samples, rather fracture toughness as an alternative analysis would be preferable.

Similarly for fatigue properties, there are differences in fatigue response for as-cast and machined SSF grades. It has been established that SSF castings retain their strength to the casting surface as-cast which is particularly an advantage for fatigue loading compared to the decarburized surface of ferritic to perlitic grades due to low silicon in the ternary Fe-C-Si alloy[12]. This property is however lost when SSF castings are machined at which time fatigue properties for comparable SSF and ferritic to perlitic grade exhibit no apparent difference. The fatigues behaviors for these two DI grades have been studied in a 4-point bending test for as-cast samples in figure 2.10[12] and similar test carried out on a steering knuckle with three different grades in figure 2.11[11,12]. The GJS-800-10 is ADI grade and has better fatigue properties but it has to be considered that an additional heat treatment is required for its production.

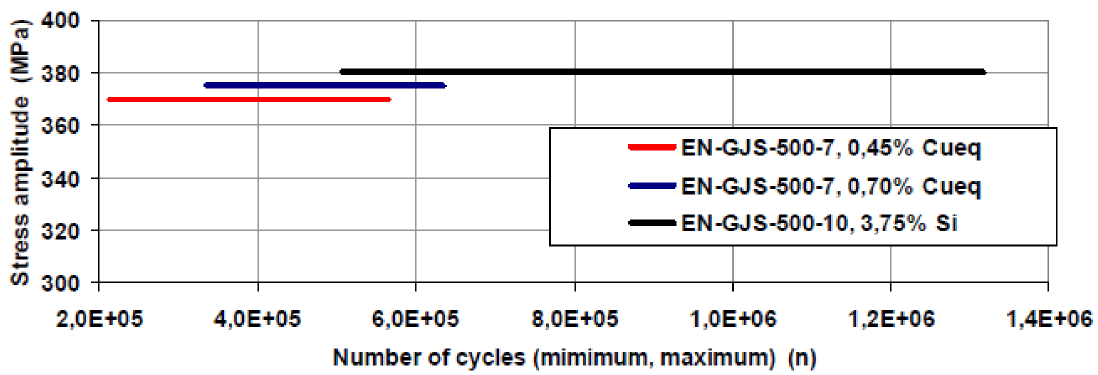


Figure 2-10. Fatigue result for 4-point bending test- Ferritic-perlitic vs SSF (as-cast surfaces) [12]

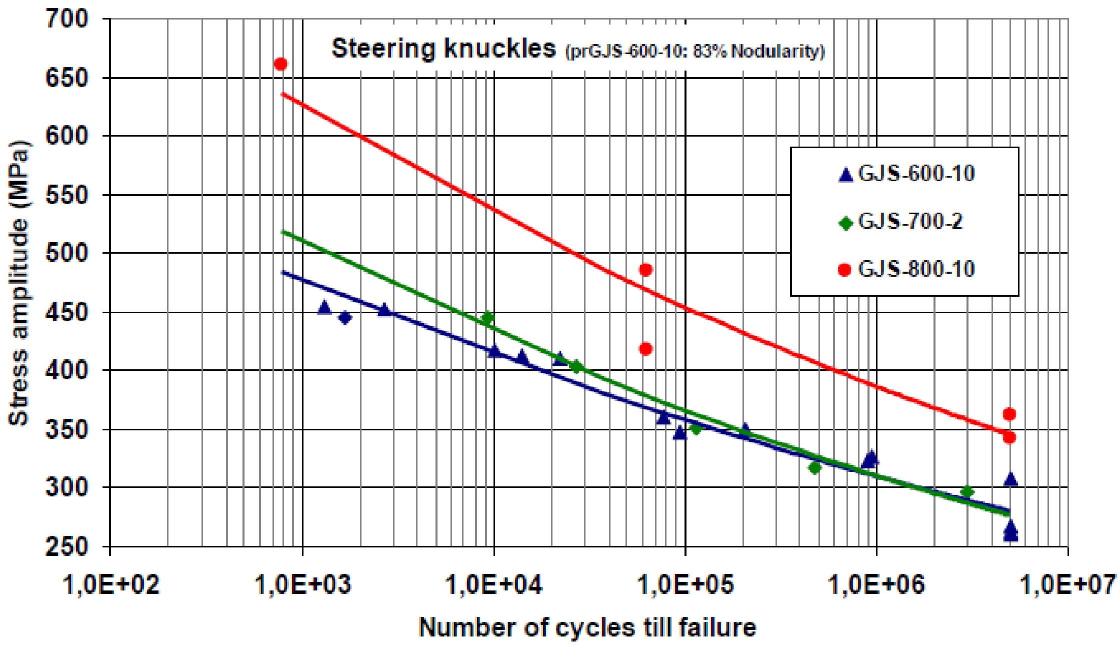


Figure 2-11. Comparable fatigue results for ferritic-perlitic and SSF grade.[11]

In spite of these commendable attributes for the SSF grades, the limit of strengthening with Si is however reached at about 4.3 wt%, (which is for the EN-GJS-600-10) when a marked decline in mechanical properties notably in strength and elongation is expereinced[3,10,11]. There have not been many explanations on why this decline occurs but few researches have offered differing but almost cohesive hypotheses suggesting causes of this decline. Part of these hypotheses include formation of long-ranged ordered crystal lattice at such high Si content in the solid solution, Si acting as embrittling element as well as segregation of Si and certain elements in the composition. These claims are all still subject of numerous studies regarding SSF grades. Other factors that have also been identified to contribute to the problem would be discussed further in latter sections of this report. While some are related to the high Si level, others to logistics and production practicalities in foundries and some to identifiable knowledge gaps about this relatively new grade. Although with the level of evidence and confidence expressed in results of concluded studies on the deterioration of properties at the high Si levels, it would be safe to speculate that strengthening limit with Si for SSF grades has been reached necessitating the need to explore other solutions to reach higher strength. Addressing challenges of SSF grades and finding alternate strengthening is central to moving beyond the current properties threshold. Investigating the alternatives nonetheless does not totally exclude the effect and inclusion of Si from consideration owing to the known outstanding properties it has already provided on current grades [2,3,7,10,] .This thus broadens the possibilities of working with and around current SSF composition. The main challenges of the SSF grades although not only limited to the Si amount has adversely culminated in some undesirable effect on strength and elongation and like in other DI grades, the amount of different alloying elements in the chemical composition also plays a role in this problem and these would be examined in the next section to create a better perception of what the properties limitations are and why they exist.

2.5.2 Influence of high silicon on mechanical properties

Upon increasing the Si content in SSF grades from the conventional 2.4wt% used in most DI grades, tensile and yield strength also increases, peaking at about 4.3wt% Si addition at which point deterioration in properties starts with the drop in tensile strength followed by subsequent decline in yield strength at 4.6wt% with both yield and tensile strength coinciding at the 4.5wt% silicon rate [10,11]. Although the negative effect of Si on elongation is well documented, it is nonetheless interesting to note that at the 4.5 wt% mark, elongation almost instantaneously drops and almost immeasurable at even higher Si addition. Most studies that have investigated the decline in mechanical properties in SSF grades argue that initial generation of embrittling elements and graphite degeneration characterized by high Si in the microstructure is in large measures responsible for the drop in tensile strength[10]. Progressive degeneration and embrittlement then leads to the subsequent fall in yield strength. The interaction within the lattice structure generated from the solid solution was also identified to contribute to intensifying rapid dislocation movement preceding the abrupt decline in properties, based on generation of long-range ordered crystal lattice. Further studies in material physics of the SSF grades would of course be necessary to corroborate these claims though. Some researchers have also opined that singular embrittling effect caused by the high Si alone[3,13] might be responsible although no decipherable reason for this has been explicitly given.

Hardness seems to be immune to the high Si content as various tests have confirmed its independence on the Si levels because hardness depends largely on matrix structure of the iron and not much with the graphite morphology. This explains why the hardness is affected neither by the embrittling effect of Si, presence of chunky graphites nor segregation of alloying elements in the microstructure[14,15]. Figure 2-12 explains the effect of increasing Si addition on mechanical properties of SSF irons. Of importance comparison are mechanical responses of SSF irons at and beyond the critical Si amount 4.3wt%.

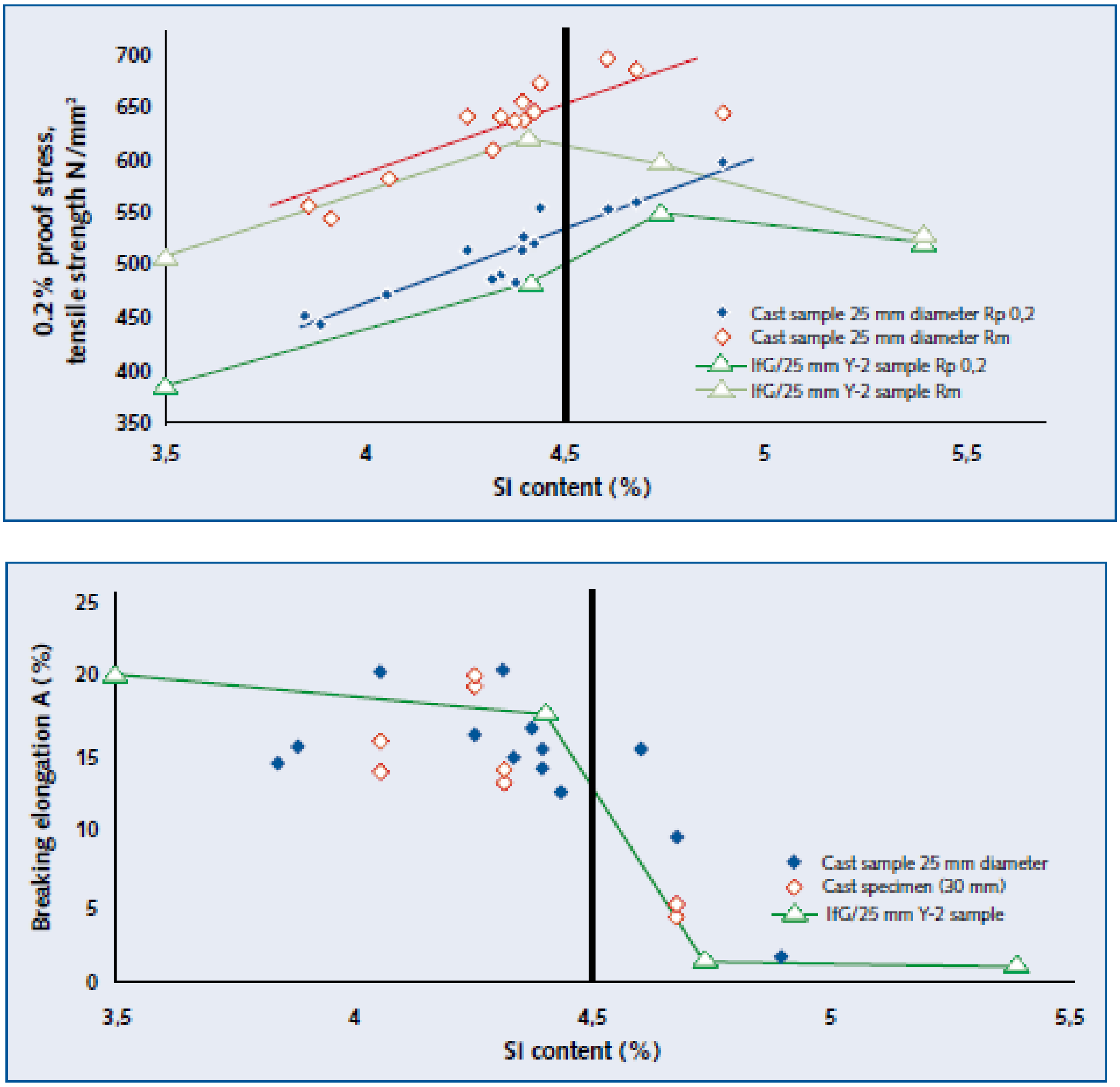


Figure 2-12: Influence of high silicon on mechanical properties of SSFs[11]

2.5.3 Chunky graphites

Graphite morphology in addition to matrix structure are responsible for material mechanical properties and determine casting quality in DI[3,14,15,16,17]. Deviation from the conventional spherical shapes in graphite nodules creates notch effect or stress concentration points in the microstructure which affects properties, although solution strengthening effect of Si reduces sensitivity to low nodularity. For the SSF grades, the EN 1563 standard accepts up to 20% non-spherical graphite in the matrix[1] with the rest recommended to be of the form V and VI as established in the EN-ISO 945-1 standard on nodule categorization. Aside from deviation from normal morphology as mentioned earlier, graphite degeneracy constitute another problem in iron microstructures affecting iron quality and properties. The most damaging of these degenerate graphites are the branched and interconnected degenerated graphites often occurring in the thermal center of DI castings[14]. They are commonly referred to as chunky graphites (CHG).

Heavy section DI castings with large wall thickness (typically larger than 60mm)[2] requiring long solidification time have in particular shown more susceptibility to CHG. The presence of this form of graphites in these type of castings especially with SSF irons have proven detrimental to properties such as ductility and UTS although with lesser effect on Brinell hardness and yield strength[14,20]. Deeply etched images from SSF cast samples in figure 2.13 reveal presence of CHG in DI casting and as manifested in the images, they macroscopically resemble a cluster of degenerated graphite in the microstructure. The existence of CHG is not entirely new to DI castings but has apparently not been discussed with much fervor until its effects on the properties of SSF grades were examined.

Different suggestions on causes of CHG in DI grades vary from inoculation practices in different foundries relating to presence of Oxygen and Sulphur in the cast to changing melt conditions during solidification to micro-segregation of alloying element in the composition. The hypothesis relating to shortage of Oxygen and Sulphur to inoculation seems credible because tests on reducing CHG through supplemental increase of oxygen and Sulphur in the melt while inoculating have recorded sizeable reduction in CHG[8]. Change in melt condition during solidification might prove to be more challenging to control especially for thicker cast sections since CHG typically form at the thermal center. More so, oxygen shortage can also be attributed to the presence of strong oxide formers like Aluminum, Calcium, cerium and other rare-earth (RE) metal in the melt.

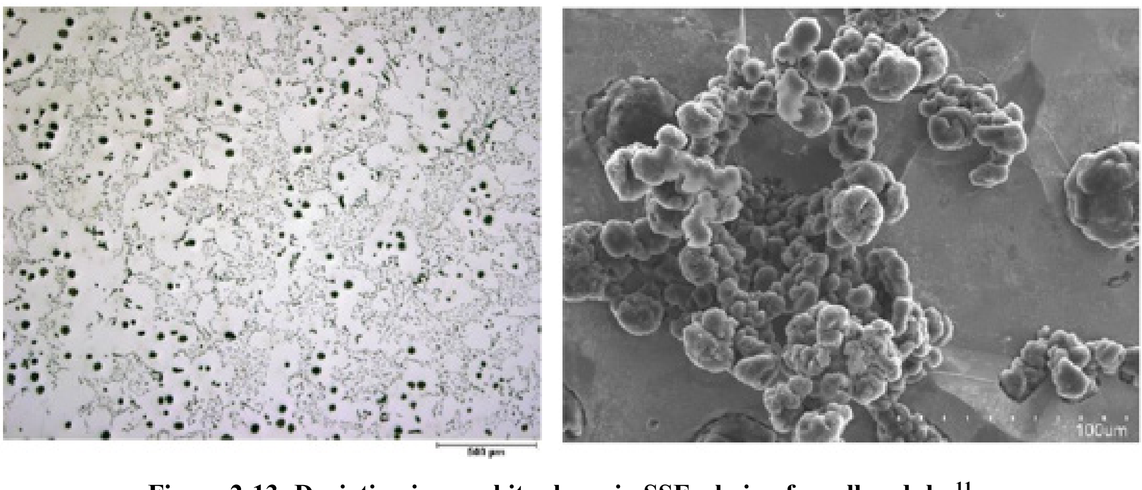


Figure 2-13: Deviation in graphite shape in SSF, chain of small nodules[11]

Studies and foundry experiences have argued that enormous mass, longer solidification time are some of the predisposing factors in heavy section castings often precipitating graphite degeneration in normal DI. This is similar in SSF castings because the high Si content coupled with foundry practices like inoculation, pouring temperature, solidification conditions and purity level of the melt all affect graphite degeneracy[10,13,17].

2.5.4 Segregation of alloys

Evaluation of current studies on SSFs and fractograph analysis from ruptured samples show mechanical resistance to failure is also impaired by Si and Mn segregation around eutectic cell regions of the iron[3,13]. Si segregates typically around the graphite nodules and eutectic cell areas while Mn is sequestered usually at cell boundaries in the analyzed SSF samples. This promotes interfacial weakness in the micro-constituents of the iron and eliminates bonding forces between the nodules and ferrite matrix as explained in studies assessing fracture patterns in SSF iron[3]. Standard casting practices offers recommendable guidelines on how to minimize these segregations but variations in foundry processes does not entirely guarantee properties in SSF grades totally devoid this problem at either production level or in compositions. Analysis of fractograph have also indicated failure pattern consistent with dislocation movement and cracks propagated at areas in the microstructure where the segregations are highest. The effect of segregated Si in DI castings is analyzed in figures 2.14 and 2.15. The test outcome of the samples shows progressive failure pattern from dimple fracture to brittle cleavage or intergranular fracture as the Si content in the iron increases[3]. Si segregation DI castings prior to the introduction of SSF grades is well known, its embrittling effect is just more prominent in SSF irons based on the high amount of Si normally required for this grade. It is a fact that other material defects like inclusions, blowholes etc. could also contribute to this pattern of material failure in castings but segregation arguably is more prone to micro-cracks initiation from relatively weakened regions in the microstructure that subsequently propagate and coalesce to form major cracks that consequently leads to material failure; this is also the case in SSF ductile irons.

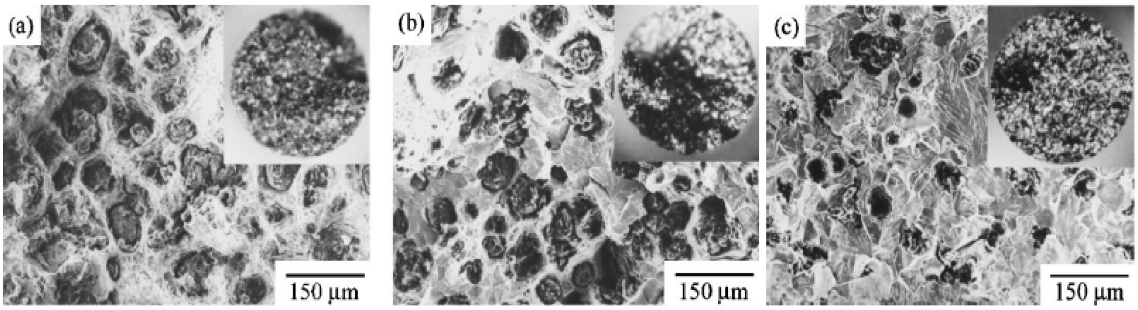


Figure 2-14. Effect of silicon on fracture pattern of DI: (a) dimple fracture (2.9Si); (b) dimple and cleavage (4.0Si); (c) cleavage (4.3Si) [13].

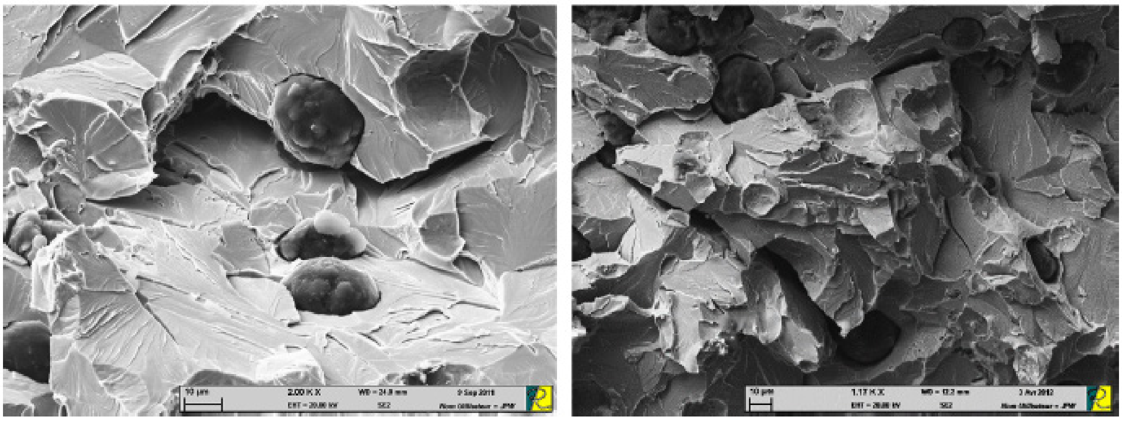


Figure 2-15. Silicon segregation- Decohesion between nodules and ferrite matrix[3]

2.5.5 Foundry Logistics and casting practicalities

Casting logistics and iron production practicalities deals broadly with foundry practices which to great extents affects the technical and economic advantage cast offer irrespective of grade or type. It is important to understand that since actual castings of thought-out cast iron designs are implemented in foundries, it is imperative that the foundry processes forms part of the design and development. Needless to say such theoretical ideas also have to have considerable recourse to what is practical or not on foundry level. There are some common logistic issues that may often impair casting quality, one of these is the capacity and production process adopted by each foundry. Foundries with smaller smelting and large holding furnace for instance face difficulties in keeping composition control and Si adjustment between batches constant[8]. This affects the C.E level and because the Si for SSF grades should be constant per grade, it reduces the cast quality of this grade. Another logistic issue is the quality of scrap metal in the iron production, many foundries use induction furnaces which are incapable of purifying the melt unlike electric furnaces hence the need for moderation in scrap quality in the melt. Extremely pure scraps would harm castings especially when inoculants containing RE metals are used while low quality scrap rich in Mn and phosphorus which are deleterious, perlite and carbide promoting elements affects cast properties. That being said, high Si in the cast composition have nonetheless been found to counter the combined effect of these two element at certain levels since controlling their levels in low quality scrap may sometimes prove impractical[3]. Also in terms of logistics, return scraps from initial castings cannot be interchangeably used for different DI grades, which creates an additional requirement and extra instrumentation for foundries to separate scraps.

Lastly, the level of knowledge and awareness concerning cast irons in general as engineering materials are still lacking compared to steels. There are multiple applications currently utilizing steels where cast irons would adequately suffice and offer comparable properties at better technical and economic advantage. This problem affects the level of researches and studies into DI and particularly, the new SSF grades.

In summary, the points discussed in this section are major challenges recognized from studies into DI production with specific focus on the SSF grade. Design approach to getting more out of this grade is to sufficiently address present challenges and formulate solutions around them. Comprehensive reviews on current studies have identified factors such as the embrittling effect of silicon, susceptibility to formation of CHG, silicon and alloy segregation as well as production practicalities as the some of the crippling factors affecting the SSF grade.

2.6 Strengthening Mechanisms

The underlying principle in material strengthening mechanism is restricting the ease of dislocation movement across the crystal structure of the metal lattice of the material. This in essence means increasing the mechanical forces required to initiate plastic deformation which is a function of microscopic dislocation movement in the lattice. Three conventional ways exist to strengthen polycrystalline metals through lattice disruption and as would be seen in their description, these methods are in fact, introduction of some form of defect into the material structure to stem the intensity of dislocation movement. The three methods *are grain size reduction, solid solution strengthening and strain hardening.* These mechanisms are suitable for single-phase metals and not typically suitable for multi-phase metals.

Other strengthening methods such *Precipitation hardening, martensitic hardening* etc. are some examples of strengthening techniques used for multiphase alloys. Practically, some of these strengthening methods like precipitation hardening are quite difficult to even implement with cast irons. Graphite structures can be severely affected by the high treatment times and temperatures that often accompany these strengthening method and also formation of elements often harmful to casting practices (-eg nodularisation) can be precipitated in the process. This and other examples of apparently negative effects of some strengthening methods on graphitic properties limits the number of available strengthening options open to cast irons compared to cast steels. The emphasis in this section would therefore be more on solid-solution strengthening with some brief introduction to other similar methods.

Grain size reduction relies on greater grain boundary area to constrain dislocation motion. Grain boundaries functionally block dislocation movement causing a huge pile up at the boundary which consequently leads to driving forces that at some point are strong enough to traverse across adjacent grains. The bigger the grain and crystallographic orientation, the larger the area available for dislocations to accumulate as driving force and propagate. Reduced grain size therefore utilizes an atomic disorder within grain boundary region resulting in lower dislocation pile up and lesser accumulation of driving forces. This effectively means larger stress level would be required to move dislocation to adjacent grains as a result of the increased crystallographic disorientation. This means higher yield strength for the material. Grain size reduction also increases the materials toughness.

Strain hardening, also called work hardening uses plastic deformation to harden or strengthen a material. The principle behind this method is that systematic application and unloading of deformable stress on the material creates groups of accumulated dislocation in the material thus increasing the dislocation density. Upon successive re-application of stresses, the material would have a resultant new yield strength each time because dislocation density increases based on a dislocation-dislocation strain relation as indicated in the figure 2.16 showing two different yield strength for a strain hardened material (σ_{yi} being the higher yield after the reapplied stress). The outcome is that dislocations repel each other due to movement in the same plane and as dislocation density rises, the repulsion between dislocations gets more evident in the strengthened material with new yield strength. The similarity between cold working and grain size reduction is that the crystallographic orientation can be restored in both methods by heat treatment while this is impossible in solid solution strengthened materials. While in contrast, work hardening cannot be typically used to strengthen cast materials. It is counterproductive in the sense that cast parts are often geometrically complex and difficult to work harden.

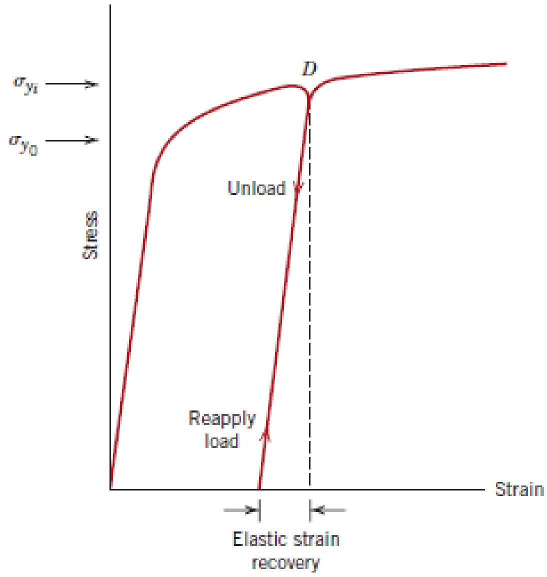


Figure 2-16. Strain hardening

2.6.1 Solid solution strengthening

Solid solution strengthening is implemented through the introduction of impurity atoms into the crystal structure of pure metals. It is one of the three alternatives available for *alloying* as a strengthening option, the other two being dispersion strengthening and precipitation hardening which are used for multiphase metals. Solid solution strengthening introduces these impurity atoms in the host metal structure either by substitution or interstitially and they impose a lattice strain on neighboring host atoms causing restriction in progressive dislocation movement in the crystal lattice[4]. These solute atoms isolates around dislocation in such manner that it relieves the overall strain energy equaling some of the strain previously induced by dislocations in the surrounding lattice.

In **substitution solid solution strengthening**, the solute and solvent atoms are typically similar in size and as the name implies, some of the solvent atoms are substituted by the impurity (solute) atoms in the lattice. **Interstitial solution strengthening** exploits the smaller size of the solute atoms to occupy interstices in the solvent lattice. Solid solutions are compositionally homogenous as the solute atoms are randomly distributed across the material matrix. Practically, solid solution strengthening depends on the solubility of the solute atoms in the host matrix and is largely affected by a number of factors to be effective. These factors include Atomic size, crystal structure, solute concentration and valence of the solute atoms (for ionic materials). The atomic size factor specifies according to Huume-Rothery rule is that the difference in atomic radii of solute and solvent atom should be less than 15% to minimize the risk of lattice distortion. It is also effective if the crystal structures of both solute and solvent matrices are similar and a high valence solute would be readily dissolved in the solvent. The solute atomic size f and volume fraction are the two most important criteria for this strengthening process and as illustrated in figure 2.17, the small and bigger solute atoms impose tensile and compressive lattice strain on the host atoms respectively. The figure also explains the relationship between the volume fraction of solute and yield strength of the material. In solid solution strengthening, the solute atoms interact with dislocations in many ways to increase material strength. The interaction could be elastic, modulus, stacking-fault, electrical, short-range and long-ranged ordered interactions[21] depending on the lattice strain imposed on the structure. Within the cast iron context and high silicon DI, solid solution strengthening uses silicon as the impurity solute in the iron melt producing a strengthened material combining unique intermediate strength and ductility. This is particularly interesting because material strengthening typically requires some compromises especially with ductility but this does not appear to be a major concern in SSF grades as they possess considerable elongation values relative to comparable standardized grades.

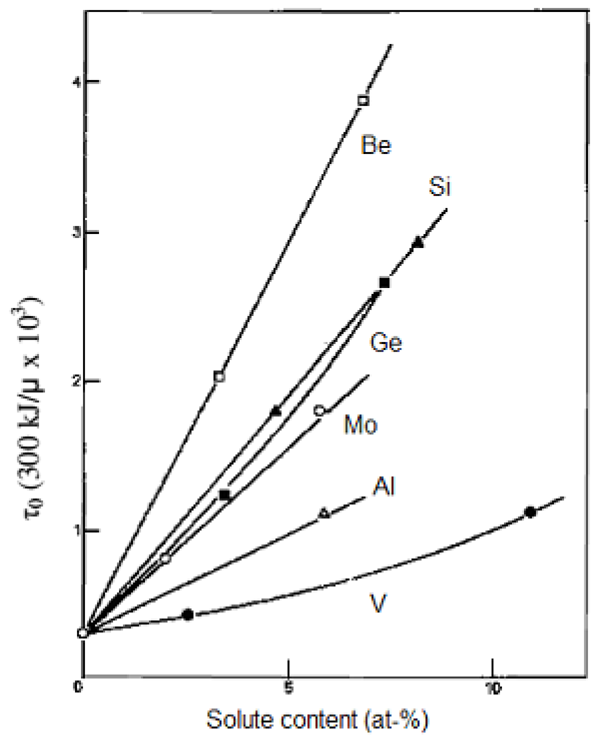


Figure 2-17. Effect of Solute content on solid solution strengthening

Other alloying methods for solution strengthening such dispersion strengthening and precipitation hardening are based on the formation or introduction of second phase materials or foreign particles which obstruct dislocation movement to improve material strength. Fiber strengthening and martensitic strengthening are also different methods for raising material yield strength but all these are suitable for multiphase materials which are not a focus in this report.

3 Literature Review

3.1 SSF grade – Literature assessment and research

The solution approach for the thesis objective is exploratory as much as novel in that it explores possibilities of reaching higher strength in SSF irons as-cast with properties besting current grades. But reaching the potentials for higher strength in the grades necessitates a critical understanding of the challenges experienced with current standardized SSF grades and limitations in properties attainable with present method of solution strengthening with Si.

Using a thematic approach in reviewing existing researches on this grade represents the core of solution strategy for information scavenging and qualitative outlook on the essentials required to understand the intrinsic potentials and challenges of the SSF grade. It also enhances the possibility to advance on improvement methods. Researches on SSF are although limited and relatively unexpansive owing to its level of maturity amongst engineering materials and market penetration. This situation is expected to and rapidly changing, judging by growing interests and better understanding of prospects of the grade. Therefore, this thesis asides its major objective also aims to supplement the information repository on the SSF grade.

This section reviews different literatures addressing topics and issues identified as sub-themes of the thesis which are sets of pertinent questions drawn up as guides for choosing relevant literatures to analyze. This approach provide better insights into the state of art in DI production, examine disparate perspectives of researchers and studies on different casting challenges of standardized grades or quality-augmentation techniques and then harmonize their inferences for a more coherent understanding of DI castings. This would supply much needed input for development strategies utilized in the ideation phase of this thesis work

3.1.1 Effect of high silicon

With respect to the high Silicon grades, major obstacles in reaching higher properties strengthening with Silicon above 4.4wt% have been attributed to the singular embrittling effect caused by the high amount of silicon, graphite degeneracy (commonly termed chunky graphites (CHG)) and segregation of some alloying element in and around the eutectic cells[10]. Characterization overview of SSFs and microstructural evaluation of the EN-GJS-500-14 and 600-10 grades examined by Stets et al, (2014) highlighted the importance of inoculation and solidification mechanism as essential tools in production of this grade. While this study does not explicitly provide decipherable reasons for the particular embrittling effect of Silicon it mentions, it appeared to suggest at such high silicon content, generation of long-ranged ordered lattice structure in the resulting solid solution aids rapid extensive dislocation movement across the microstructure resulting in abrupt material failure. Hung-Mao et al (2003)[13], similarly concluded that the rate of embrittlement experienced in ductile iron is proportional to the increase in silicon content. Evidence for this assertion was presented in the form of fracture patterns seen on different ductile irons tested with increasing amount of silicon ranging from dimple failure to brittle cleavages. These modes of failure pattern are representative of ductile and brittle fracture respectively. Furthermore, it was suggested that the presence of inclusions and segregation of oxides of magnesium or cerium in the eutectic cell boundaries further assist the action of Silicon in the evaluated fractograph.

Likewise Larker (2009)[8], provided proof that while silicon-rich DI fare remarkably well at elevated temperatures and thermal cycles because silicon raises the eutectoid temperature, they are also affected by the Silicon content at these stages.

Other challenges encountered with SSF grades identified in this study included the presence of CHG, dross formation and susceptibility to porosities. Similar results were also reported by Duit (2013)[2] from casting experiences with SSF irons. The report further suggested lesser dependence of mechanical properties on nodularity in SSF grades compared to first generation DIs because nodule shape or graphite morphology allows the matrix structure determine the mechanical properties of the iron.

Alhussein et al,(2014)[3], comments that increased silicon does not affect average grain size and that the combined effect of Silicon segregation and casting defects is most responsible for the drastic change in ductility and material resilience at high silicon contents. Using consequential evidences from observing microstructures and failure patterns of high-silicon irons, the study explained the importance of composition on the initiation and propagation of cracks in SSF grades. Macro-segregation of silicon close to the graphite nodules causes decohesion between the nodules and matrix during yield because this level of segregation does not offer much resistance to propagation of dislocation. Larker (2009)[8] provided evidences of very comparable impact energy and slightly better fracture toughness between SSF and ferritic to perlitic grades of equivalent strength. Due to a homogenous ferritic matrix structure precipitated by solid solution strengthening effect of Silicon, SSF grades have very low hardness variation which translates to better machinability compared to the ferritic to perlitic grades. From a production point of view in foundries, this improves dimensional accuracy and geometric control easier. Bjorkegren and Hamberg (2003)[18] and Herfurth (2011)[19] agreed with these conclusions and Herfurth et al explored further on the theoretical links between the highly homogenous hardness distribution in SSF castings, solidification and cooling conditions through different forms of castings. It was inferred that continuous castings as opposed to sand casting provided better cooling conditions favorable for SSF grades, especially heavy section castings traditionally prone to graphite degeneracy. The results of this method constituted preemptive studies for casting the GOPAC C500 F[19], a highly pressurized hydraulic blocks presented in the research.

3.1.2 Effect of chemical composition

The richness in Silicon is not solely responsible for both enhanced properties and challenges in SSFs, studies have also shown that present limitations in properties can also be related to influence of other elements in the chemical composition or subversive trace elements present in scraps used in the casting. Selection and priority of elements in the chemical composition is key to moving beyond current property thresholds of this grade (Serrallach et al, 2010)[20].

Production of ductile iron through an adequate balance of alloying elements can more than adequately substitute heat treatment and mechanical properties obtained through this method according to results obtained from the works of Gonzaga (2013)[16], Gonzaga and Carrasquilla (2005)[21] are often better than those obtained through common methods. It is quite pragmatic to also draw inspiration for improvement ideas from enhancement techniques in other engineering materials for applicable method for the thesis goal. Steel production and super alloys are interesting areas to look into considering how these super alloys have in a relatively short time became almost ubiquitous in aerospace, energy, chemical industries and even medicine. Combination of excellent mechanical properties, corrosion resistance and bio-compatibility renders these alloys the best material choice for many critical applications[22]. Strengthening mechanisms through controlled alloying is a popular concept even in steel production.

Gonzaga (2013)[16], Gonzaga and Carrasquilla (2005)[21] clearly pointed out that graphite nodularity governs yield and fracture elongation and identified the deleterious effect of excess manganese (Mn) and phosphorus (P) on ferritic ductile irons. With a similar research outcome, Riposan (2007)[23] also recommended that less than 0.03wt% P and no more than 0.2wt% Mn are optimal percentages for both elements in chemical composition to obtain as-cast ferritic structure in DI. Nonetheless, according Gonzaga and Carrasquilla (2005), high silicon in DI nullifies the combined adverse effect of Mn and P in the composition[3,16]

One of the primary features of typical compositions for DI is that it is constituted to reduce the probability of carbide formation, volume fraction of ferrite or perlite in the microstructure depending on the desired matrix, as well as the graphite properties. While these conditions as mentioned before could be met with appropriate choice and amount of elements in the composition, there are secondary factors like inoculation and solidification sequences that also contribute and should be controlled to get the best quality castings (Serrallach et al, 2010[20], Gonzaga (2013)[16]. Getting either of these factors wrong affect the outcome and mechanical properties of the casting.

3.1.3 CHG and solidification mechanism

Occurrence of chunky graphites in the microstructure is one of the marks of these aforementioned factors, although it is relatively unclear which of these factors considerably influences this form of graphite. CHG is one of the least understood phenomenon in casting as there still exist no unified theory addressing its formation or definitive combative measures. Different researches have discussed its causes and proposed preventive actions but these are based on their respective angles of study and research scopes.

For example, Källbom (2005, 2006)[15] on solidification sequence in ductile iron attributed the presence of “degenerate” graphite in the microstructure to solidification mechanism used for individual castings. Since spherical graphites were present in the last solidified areas, it was argued that that chunky graphite forms early during the eutectic solidification. The study went to propose that the volume percentage of chunky graphites present in the microstructure influences in measurable amount the decline in ultimate tensile strength and fracture elongation of the casting[14]. Correspondingly, Muhmond & Fredriksson (2013) also believes this form of graphite in high-silicon DI showed low graphite nucleation potential caused by the absence of Oxygen and Sulphur in the affected areas. The presence of Sulphur and Oxygen in the melt is a quite complicated topic in relation to graphite growth morphologies in cast irons. In DI for instance, nodularizing agents like Magnesium and inoculants influences the presence of these elements which subsequently affects transition in graphite morphology[24]. Supplemental addition of S and O to reduce shrinkage, chill (carbide formation), sustain continued graphite nucleation and growth for high quality DI casting was suggested by Skaland (2009)[25] arguing for the use of inoculants containing rare-earth (RE) metal for DI castings. Using RE metals inoculants should however be a function of the purity level of the scrap metal because excessive amounts in high purity scrap will promote formation of chunky graphites[26]. These studies are indication of the role of Sulphur and Oxygen in graphite characterization in cast irons. As with most elements in the composition, Sulphur and oxygen at moderated levels post-inoculation promotes suitable nuclei for graphite precipitation with positive effects on nodularity (Riposan et al, 2003)[27]. The implications of these studies purporting the continual supply of Sulphur and Oxygen could be vital to solving the presence of CHG in the microstructure. Low graphite nucleation potential could be addressed through supplemental addition post-inoculation experimented in the works of Skaland[25,28] to reduce the occurrence probability of CHG. More so, In spite of the higher Carbon and Silicon in ductile irons, the shrinkage and chilling tendencies in ductile iron is more than in other types of cast irons which is largely due to difference in graphitization during their respective eutectic solidification. Contrary views on the formation of CHG was the time-dependent thickening of the austenite shell in DI which inhibits continuous nucleation of graphite due to low carbon diffusion rate causing lesser and possibly larger nodular graphites. (Nakae, 2007)[29]

Larranaga et al (2009)[30,31] in agreement with Nakae (2011)[32] proposed that in castings with Cerium, stringent control of cooling and addition of higher amount of Antimony (Sb) in a proportionate ratio will improve properties of such casts. In castings where RE metal inoculation is used, addition of Sb or other anti-spherodizing elements was found to balance out the negative effect of RE metals especially in high-purity melts and large section casting[33] since concentration of Sb or lead (Pb) around the graphite was expected to stop impending degeneracy. The study notwithstanding does not give compelling evidence that this measure effectively nullifies the presence of CHG because Sb if not controlled in the composition is known apart from being a perlite promoter to also cause further graphite degeneracy. Zhe, 2012[34] expounded on this idea with focus on how the effect of Sb in the composition can be influenced by cooling rates. From evaluated cooling curves, it was established that since graphite deteriorates between 1,170 ℃ to 1,080 ℃ during solidification, slow cooling rates plus an optimal ratio of 2 between Sb and RE metal would prevent the occurrence of degenerate graphites.

3.1.4 Cooling rates and strengthening

Baring the problem of CHG in thin and heavy sections castings, the effect of cooling rates on solidification of cast irons in both are quite similar given similar chemical composition and casting parameters. In relation to their cooling curves, heavy sections differ with a longer eutectic plateau. The cooling curves confirm that cooling rates affect solidification time of the eutectic transformation and that characteristic temperature points on the cooling curves remain unchanged[35,36]. The nodularity and nodule count is also found to be dependent on the cooling rates of the castings[34,36] which of course are also exemplified in graphites characteristics of DI with perlitic matrix when fast-cooled. Liang et al, (2015)[37] studied the effect of silicon on mechanical properties of heavy section DI but the effect of cooling rate was rather more apparent from the study. The presence of quasi-spheroidal, vermicular and chunky graphite is result of decreasing cooling rates and insufficient nucleation during solidification of these heavy sections. The proof presented in this study purporting the presence of CHG in the last solidified section is in contrast with views held by Källbom (2006)[15] that formation of CHG precedes the spheroidal graphites. It was further outlined that cooling rate in heavy sections affects graphite properties and consequently, mechanical properties of the silicon-alloyed DI. The reasoning here is that the cooling rate is a function of the casting's section modulus and heat removal rate which are both dependent on mold geometry, material and pouring parameters. This accounts for the variation in mechanical properties governed by matrix structure in different sections of the same casting (Shinde, 2012)[38].

Elements such as Bismuth (Bi), Aluminum (Al), Boron (B), Tin (Sn), Copper (Cu), are acknowledged to prevent the formation of CHG[15,37,39] but with complications being either anti-spheroidizing agents or perlite promoters which in the case of DI are undesirable.

Besides the basic composition in DI described in the first section of this report, selection of additional alloying elements are based on the role of the elements on the intended properties of the cast iron. Carefully assessing the properties of chosen element to alloy has to be relative to the base composition either individually or in combination. Cho et al (2007)[40] detailed visible changes in nodule count, graphite morphology and volume fraction of ferrite to perlite in tests administered with Mo, Cu, Ni and Cr as alloying element to pure DI melt. It was possible to even get a different matrix structure and graphite properties at different alloying contents of the same element.

Comparable with the scope of this thesis, Hsu (2007) examined the role of alloying as an alternative to heat treatment on mechanical properties of as-cast DI using ferrite and perlite promoting Cobalt (Co) and Nickel (Ni). Using a mathematical model relating tensile strength and elongation by Siefer (1970) it was maintained that solution strengthening by Co produced up to 45% increase in nodule count with a dominant ferritic matrix. Strength values also more than doubled those in compared unalloyed DI. The result showed that Co plays an important role in stabilizing the ferritic matrix with increase in nodule count. Shen et al (1995)[41] equally declared that Co improves graphite shape and increases the nodule size but does not typically improve nodule counts especially in small additions. The disparity between these two studies coming from the effective alloying content of Co. Homogenous solubility of Co in the DI matrix makes it a lesser segregation risk with fractograph showing mixed fibrous flow and cleavage facets on the fractured surface supporting a mix of ductile and brittle failure.

While the role of cobalt in ductile iron production is far from fully understood, a discernible conclusion from many researches is that noticeable effect of Co are usually at high alloying amounts.(Shen et al, 1995).

Properties relating to strength and elongation diminish as the percentage of non-nodular graphites increase as well as decrease in nodule count and larger size. Likewise, hardness and impact toughness are influenced by the matrix structure[3,6,16,21,42]. Niobium as an illustration may increase nodule count but its effect on nodularity negatively affects elongation while positive effects on strength and hardness can be traced to the formation of stable carbides[43-45]. Niobium alloying was more popular in steel production before being introduced in cast irons. While this element would offer tremendous properties in wear resistant or hard castings, for DI It is necessary to minimize carbide levels as it will often segregate strongly and affect ductility. Similar trends were observed alloying with Vanadium (Vn)[41].

3.1.5 Effects of Inoculation and scrap quality

Casting practicalities like inoculation and scrap quality also constitute integral parts of the production process for DI castings. Different forms of inoculation and inoculants are suited to different castings and thus the choice of inoculant and scrap should be permutated against each other and the chemical composition. Typical elements such as Zinc (Zn), Al, Cu, Cr, Pb, or other trace elements could be found in the scrap depending on application or industry they originate from. For Instance, magnetic steel scrap are rich in

Sb or Mn while Carbon steel scrap rich in Sn are unsuitable for DI castings. It may be quite challenging in some cases to accurately quantify exact amounts of constituent elements in the scrap as even trace amount of contaminable elements could disrupt desired cast results.[46].

The choice of inoculant and the inoculation sequence are often based on foundry practices and experience with individual cast iron grades. Most studies into inoculation practices, for example for SSF grades have so far been centered on solving CHG which is very understandable. Inoculant choice and timing has to consider both chemical compositions of the inoculants and that of the melt charge. The inability of most researches to clearly distinguish between these factors form the major reason in disparity on result of studies into inoculation (Asenjo et al, 2007)[47]. Stets et al.(2014)[10] proposed the use of Bismuth (Bi) inoculant containing RE metal to avoid CHG having recorded better result in tests using this inoculant. (Ferro et al, 2013)[33] substantiated this claims affirming the positive effect of Bi inoculant containing RE metals on preventing CHG and promoting as-cast ferritic matrix structure. The absence of CHG was attributed to reactions of Bi with O, S, and P while stabilizing the austenite shell around the nodules. It should be noted that Bi above certain levels could also have detrimental effects on nodularity as a result of its interaction with Magnesium.

The inclusion of RE metal in inoculants is further backed by proof of its action on the deleterious effect of subversive trace elements in the melt and creating additional nucleation sites for the graphites which particularly helps with controlling shrinkage and chill formation in the casting. Besides the type of inoculant used, many analyses have equally favored post-inoculation practice in addition to ladle inoculation, especially in heavy section castings. The advantage of this method as enumerated by Skaland (2001) and Olssen (2004)[7,48] is that it reduces the adverse results caused by fading, particle coarsening and minimizes deleterious effect by increasing nodule count and reducing the degree of segregation. Cabanne and Gagné (2010)[49] yet while confirming these benefits also view post-inoculation as an expensive precautionary step rather than an actual inoculation practice. It was contended that despite using lesser amount of inoculants required for late inoculation, there are still serious risks of contaminating the mold sand which then results in defective castings when reused or inoculant spillage around the pouring basin.

Summarily, from the different themes in the literatures reviewed, three conditions appear as apparent prerequisites for high quality castings. These conditions are 1. Stringent choice and control of chemical composition based on desired properties, careful selection and quantification of scrap charge and Optimizing casting parameters based on the previous two conditions. These three steps form a logical production process that put the foundry in charge of all controllable parameters in the production chain. While extra attention must be paid in cases of different alloying according to customer requirements, these steps still work as major rule of thumb for all castings.

3.2 High strength SSF – ideation

The thesis objective is to develop a high strength SSF iron and in line with the adapted solution strategy, this section describes the ideation and development process used to achieve the thesis goal. Harmonized inferences from the reviewed literatures and design thinking methods are the two most important tools used in this ideation. As mentioned in the introductory part of this report, the intended outcome of this part of the work breakdown structure will be a chemical composition comprising alloying elements that support and propagate material properties for identified parameters influencing high strength in DI. Projection for the intended high-strength SSF would be to top the EN-GJS-500-14 or EN-GJS-600-10 SSF grades in either tensile strength and/or elongation.

With the different parameters governing desired mechanical properties for high strength iron in mind, the next logical step was to decide which alloying elements and in what optimal quantity supports these identified parameters, while analyzing their effects individually and also relative to other elements in the composition. Figure 3-2 describes a schematic of the identified material parameters (in blue outline) supporting high strength DI and how they influence material properties.

The proposed chemical composition would thus be a combination of basic SSF composition plus possible options of alloying elements based on the schematic in figure 3-2. It is necessary to also mention that the created options of alloying elements from the schematic and final chemical composition are tentative results that still depend on casting processes and secondary production factors like inoculation or casting methods in the foundry. This means the development process in this section is done with utmost reflection of what is possible in practical situations in foundries.

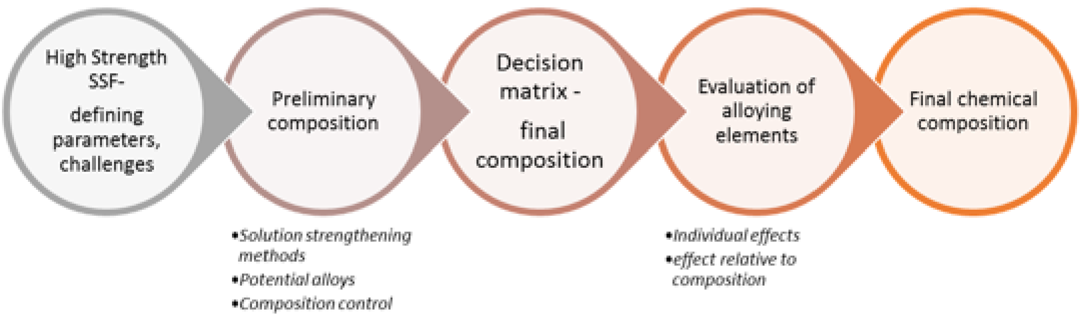


Figure 3-1. Process steps for developing composition for high strength SSF

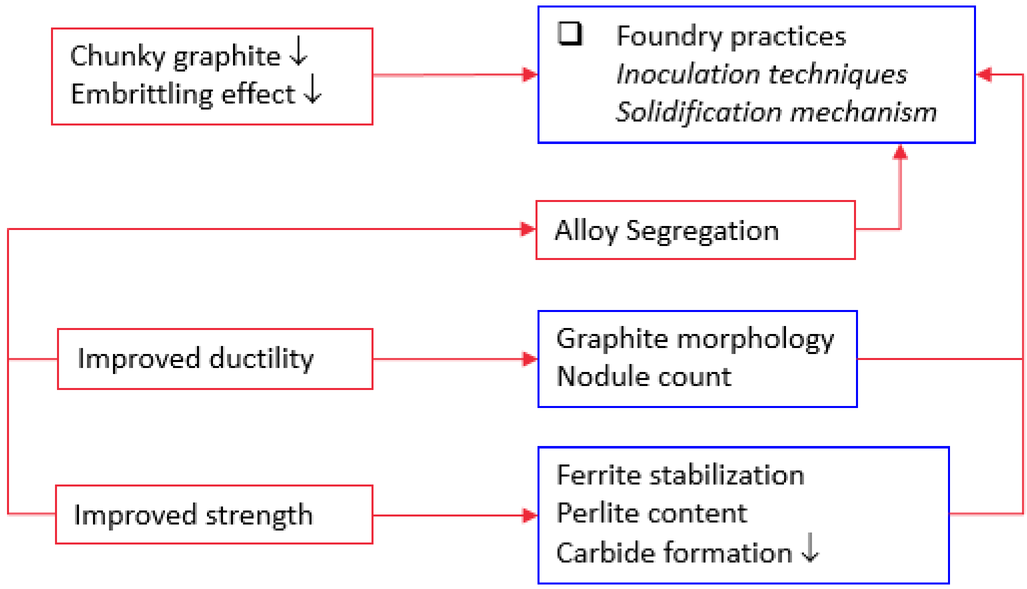


Figure 3-2: Material parameters to influence high strength in SSF irons

Expectedly, there is a huge bank of potential alloying elements fitting preliminary requirements for some of these identified parameters for higher strength in DI. To narrow down the huge number of elements down to more veritable options, more specific details in the DI specification like its ferritic matrix and grade were matched against properties of each element. The remainders are then further reduced by considering their properties and performance against the identified parameters for high strength SSF as described by step 1 in figure 3-1 showing the process steps leading to the final composition.

3.2.1 Chemical composition

Step 1. – The EN: 1563 standard typically specifies parameters and properties defining the SSF grade but within the scope of this thesis work, these specifications are loosely followed to avoid limiting the creative solution space for the intended objective. However exceptions to this limitation are specifications on Silicon amount and graphite properties, considering their importance to the SSF grade. The step 1 of the ideation process therefore involves consideration and elimination of different elements against required parameters for the intended high strength iron with considerable recourse to specifications from the standard.

The step 2 involved assessment of preliminary basic composition for EN-GJS-600-10 grade since it will be both reference and base iron for the intended high strength SSF iron. It was only sensible to aim higher from the best of the current SSF grade. The final composition range and percentage amount of individual elements in the chemical composition of the base EN-GJS-600-10 used in the experimental irons would be adjusted accordingly relative to the chosen strengthening alloy(s) and calculated CE. In practice, foundries can usually adjust their basic compositions as long mechanical requirements of the standards are met. Highlight of the activities in this step of the ideation was composition control which basically translates to determining appropriate alloying percentage of each element in the chemical composition for both the reference 600-10 and experimental irons.

This composition control is essential when alloying as strengthening mechanism is used because the introduction of new “alloying element(s)” generally affect the compositional balance for conventional or existing “host composition”. Prior consultation with the foundry at this stage plus knowledge of the foundry’s manufacturing processes and scrap supply was important. This enabled necessary adjustments in the choice of alloying elements in the chemical composition for better feasibility assessment.

Table 3-1. Initial Basic composition for EN-GJS-600-10

Melts	Carbon C	Silicon Si	Manganese Mn	Sulphur S	Phosphorus P
A	2.80 – 3.50	4.30	< 0.30	< 0,02	< 0,03

Step 3 of the ideation process involved the creation of a decision matrix based on certain set criteria for high strength in DI. Table 3-3 outlines the decision matrix table considering elements against high strength parameters. These assessment criteria are basically material properties’ indicator supporting identified parameters for the intended high strength iron. While the remaining elements up for consideration all possess veritable potentials as strengthening alloy, these criteria in the decision matrix with differing priority levels offers better scrutiny to eliminate options short of desired requirements.

For instance, an element which promotes a ferritic matrix as-cast with better microstructural effect is prioritized over another which provides better strength at lower ferritization potentials. Reaction with major composition elements like carbon and silicon are also placed higher.

Elements such as lead (Pb), Titanium (Ti), Aluminum (Al), Zirconium (Zc), etc. which are expressly known to promote flaky graphite or Calcium (Ca), Tin (Sn), Vanadium (Vn), Molybdenum (Mo), Chromium (Cr) etc. known as strong pearlite formers and/or carbides promoters were not considered in the overall elements frame to reduce the burden of going through options devoid of actual high strength potential in DI. However since the standard still permits up to 5% perlitic content for the SSF grade, mild perlite promoters were considered to exploit the additional benefits of the extra perlitic content in the experimental Iron. Ni for example, decreases primary carbide stability while improving the fineness of perlite, it increases the strength of the Iron[17]. Table 3.2 shows the proposed composition based on the outcome of the ideation. The table comprises three different compositions with the melts A, B and C representing the reference EN-GJS-600-10 SSF grade plus variations with 2% and 4% Co additions respectively. The melts B and C are necessary to evaluate the level of influence Co would have on mechanical properties.

Table 3-2. Chemical composition for intended high strength SSF

Melts	C	Si	Mn	S	P	Co	CEv
600-10	2.88	4.30	0.30	0.02	0.03	-	4,32
B	2.88	4.30	0.30	0.02	0.03	2.00	4,32
C	2.88	4.30	0.30	0.02	0.03	4.00	4,32

CEv% = %C + %(Si + P)/3

Alloy Element	Microstructural influence	Graphite properties	Nodule counts	CHG or carbide formation	Segregation potentials	Solubility	Notes
Cu	Promotes and stabilizes pearlite in combination with C. For ferrite matrix < 0.03%	Typically >85% nodularity, medium	Fairly high	Insignificant	High	Highly soluble in austenite. Solubility also depends on carbon.	Cu without the presence of Mn support ferrite but below 0.6wt%. segregation of copper is related to the decrease in diffusion of carbon through the ferrite shell
Ni	Promotes pearlite but does not stabilize it ferrite depends on content	Up to 90% nodularity.	Low	Insignificant	High	Homogenous Dissolution into DI	In cases where as-cast ferrite is desired; Ni should be avoided. Machinability of cast iron is easier with Ni then Cu
Co	Promotes graphites and stabilizes austenite	Up to 92% nodularity and smaller nodules	High	Inhibits CHG	Low	Excellent Dissolution	Effect of Co has been more documented in steel production with equal amounts of Ni. Immense with toughness
Cr	depends on nodule counts to promote perlite	insignificant	none	Promotes carbides	Low Segregates to cell boundaries in heavy sections	Good dissolution	This implies that the action of chromium in ductile iron depends on the contents of carbon and silicon.
Sb	Depending on content, promotes perlite or supports ferritization	~ 90% And Small nodules (depending on cooling rate)	Fair	Inhibits CHG and carbides formation	-	Good	Tests have shown that ~0.03wt% is optimal amount needed. Useful in heavy section castings but imbalance with RE inoculant creates anti spheroidisation.
Nb	Negative effect on ferrite, mild perlite promoter	Insignificant	Insignificant				

Table 3-3: Decision matrix for potential alloying elements.

3.2.2 Strengthening Alloy - Co

Based on influencing factors tabulated for the considered elements shown in table 3.3, Cobalt **Co** offered significantly better option to test than Antimony **(Sb),** which also deemed a good fit for the experimental purpose. Within Cast iron production, the use of Co in any capacity is not very common and thus much of the inspiration in its addition into the alloying elements consideration frame comes from its use in steel production.
Examining applications typically utilizing Co alloying, one common trend is the high alloying amount, with common examples in the aptly-termed super-alloys[50] which acquire their excellent properties from solid solution strengthening.
Ferritization potentials for Co are immensely good, not only for promoting ferrite in the matrix but also particularly its ability to stabilize austenite leading to increased ferrite production. To obtain sound castings, the Si level must be balanced with C level which is very often an important aspect in the high silicon DI but Co has been found to lower the C content in the original austenite[51].
The effect and benefits of Co in solution strengthening is however key to the development aimed for in this thesis work considering the requirement of having a high strength iron as-cast and aligning it property-wise with the SSF grade. Co with similarities in attributes to Si and its relative chemical passivity in the chemical composition provides an experimental iron aligned and improving on properties from the base iron. This in effect implies that an experimental iron with improved properties can be expected from the base 600-10 iron with significant semblance to the SSF grades.
Co offers better resilience to fracture with positive segregation to intercellular boundaries during solidification compared to Si, this particular property is exploited in the use of Co in ADIs to accelerate stage one reaction in austenisation resulting in shortened austempering time and options for thicker sections[51].
Typically with high nodule counts and smaller eutectic size, toughness properties have been found to improve with Co alloying in most examined cases from both Cast iron and steel applications. Although there has not been many studies verifying high strength in DI with Co, its solution strengthening effect and positive microstructural effect is expected to support high strength in the casting. Possible compromise on ductility or nodularity rating would nonetheless have to be determined from tests on the casting outcome.

3.2.3 Recommendable casting practices

While this section does not necessarily try to change conventions about castings or usual practices with different foundries, it aims to give some insight into favorable supplementary practices that could enhance foundry experience while handling SSF castings. The suggestions given represents combination of different recommendations from numerous researches into how the practical issues in foundries can influence the casting quality for high silicon ductile irons.

The difference in type of casting has been noted to also have a bearing on the casting outcome but sand molds are more instrumental in getting a good cast and also a good option for SSF irons especially in cases where complex castings with large variations in section size or constrained thin sections. These types of sections are very prone to residual stresses which can be relieved using sand molds, although usually the occurrence of residual stresses could be handled with good casting designs. Likewise, premature shakeout can subsequently induce residual stress in the cast even when sand casting has been used and also cause hardness variation across the sections[52].

The inoculation method used for castings depends on foundry's experience and also on type of casting but traditionally, commercial inoculants have been based on ferrosilicon alloys containing metallic additives such as Calcium, Barium, Strontium, Aluminum, Zirconium, Rare Earth's, etc. But with SSF irons, susceptibility to CHG may however warrant a slight change of direction on conventional inoculants. With restricted availability of Sulphur and Oxygen in the iron, performance of metallic inoculant additives would be limited when their effectiveness are restricted by the number of potent nucleation sites from after inoculation[7]. Hence the choice of inoculant and application method should be determined by the quality of scrap metal used and desired properties or geometry of the casting. For instance, the presence of RE elements in high purity scrap can be unnecessary and even lead to CHG. Bismuth containing inoculant for both thin and thick section and Ca-Ce-containing inoculants for thin sections SSF irons have returned good results in recent tests.

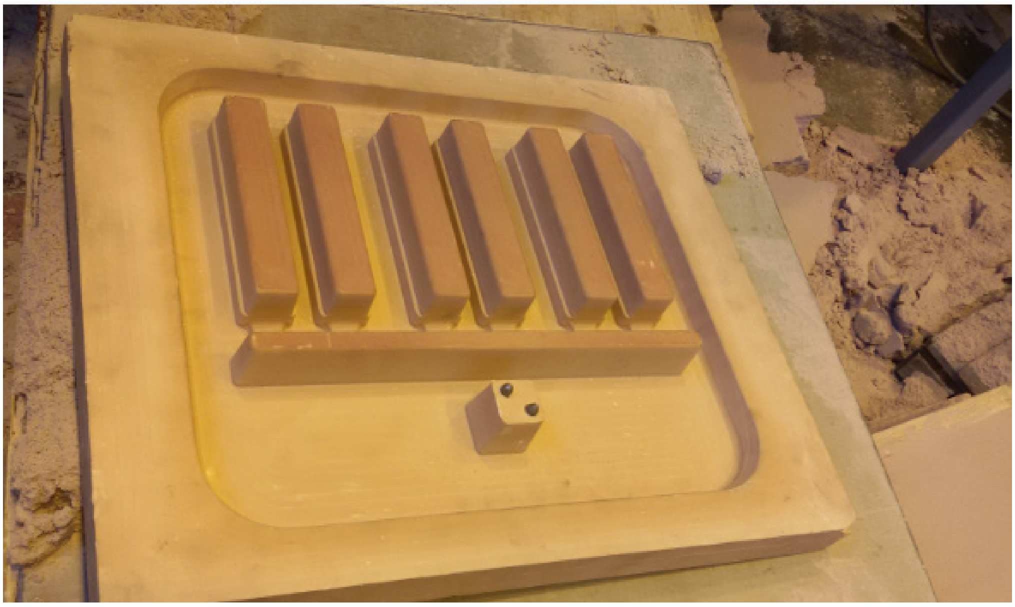
4 Experimentation and casting trials

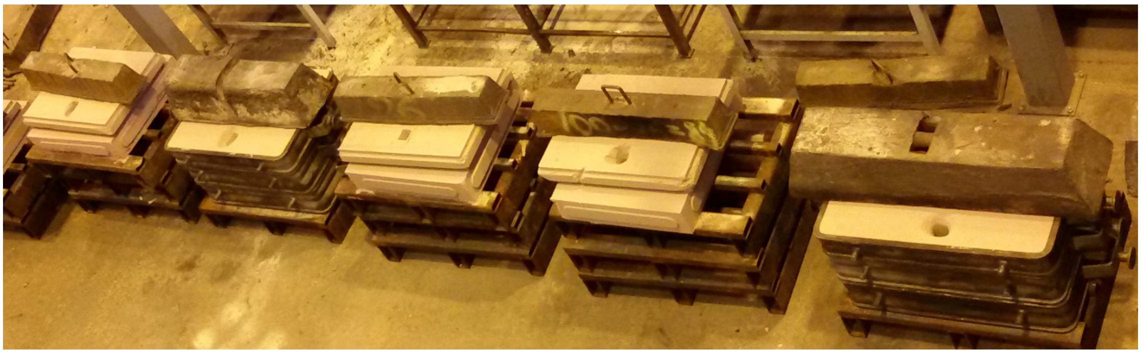
This aspect of the thesis work schedule represents the most important part because it examines the feasibility of the thesis idea and validates claims from reviewed literatures. Based on the decision to alloy the SSF composition with Co, casting trial of the experimental alloys plus the reference basic GJS-600-10 composition was carried out to evaluate the feasibility of this Co alloying on mechanical properties to reach high strength. While the ideation has provided a target composition for both reference and experimental irons, it is important to understand that spectrometric analysis of samples from resultant castings ultimately determine final alloying amount of elements in the composition. Particular interest in this scenario would be exact quantity of Co successfully dissolved in the melts. This and the results of microstructural and strength analysis formed the basis for conclusions and inferences that would be drawn from impact assessment of the elements in the chemical composition.

The experimental alloys designated melts A, B, C representing compositions for EN-GJS-600-10 and 2% -Co, 4%-Co experimental irons with compositions as outlined in table 3-2 were melted and cast at ValimoInstituutti Foundry, Tampere. The melting was performed in a 300kg induction furnace using steel scrap with composition shown in Appendix 1. The melts were superheated to the casting temperature of 1510^{o}C by the induction unit during which controlled addition of alloying elements were introduced into the furnace.

Magnesium treatment with ferrosilicon (Fe-Si-Mg) using Elkem’s “Lamet” containing (Calcium and Lanthanum) was carried out in the ladle using the sandwich method. This type of Nodulariser is well suited for both in-the-mold and ladle treatment of DI preventing shrinkage. The melts were then subsequently inoculated using foundriSil (Si-Ba-Ca-(Al)). Full technical specification of these inoculant and Nodulariser are shown in Appendices 2 and 3 respectively. Covering flux was sporadically added to the melt to fix dross formation and then skimmed off prior to transfer to the pouring ladle. The ready melts were then transferred to a pouring ladle before filling the dry sand molds (a 30mm diameter tensile bar mold and a Y-block mold) at 1460^{o}C. As stated before, in order to create equal conditions for all three iron castings, the basic melt (GJS-600-10) was the same for all three casting, the melt B and C only differed with the varying percentages of cobalt added.

After pouring the required quantity for the base melt 600-10 into the treatment ladle, 2wt% Co was added to the ladle for melt B and upon extracting the needed quantity, an additional 2wt% was subsequently added to make up the 4-wt% Co for melt C and poured into respective molds. Creating the three castings from similar melt conditions provides a strong basis for comparative analysis against each other and a more cohesive conclusive evidence to support test response. Figure 5.1 outlines a brief process schematic of the casting methods described in earlier section.





5.1(b) Melting Furnace

5.1(c): Transfer from the melting furnace to the pouring ladle

5.1(d): Addition of covering flux to the pouring ladle to fix dross formation

Figure 4-1: Filling the molds for the experimental alloys¨

4.1 Material preparation and properties characterization

Prior to filling in the molds for the three irons, samples, fast-cooled in a small permanent die to solidify as white cast iron were taken for spectrometric analysis to determine the final composition of the castings. This is particularly useful to ascertain if the intended chemical composition was achieved. For the Co- alloyed iron samples, the spectrometric analysis accurately showed 2% and 4% Co as intended dissolved in the castings for both melts B and C respectively while the reference 600-10 melt returned spectrometric values as intended also. Due to miscommunication during the casting trial, samples from the Co-alloyed irons were not taken immediately and so spectrometric analysis on these had to be done later. Since graphitic structures cannot be sufficiently analyzed using optical emission spectrometry (OES) methods, samples for the Co-alloyed irons had to be re-melted for its spectrometric analysis. Re-melting however poses considerable challenges in alloying elements retention capabilities thus acting as catalyst for reactive elements in the samples which advertently affect the analysis. But elements like Co are not affected by this because it is highly stable element. Therefore, the final spectrometry for the Co-alloyed irons was combined with that of the 600-10, to give a combined reading from the analysis. And also since the same base melt is used for all three irons, there is enough credibility for this approach even considering the very minute change the Co alloying may have introduced. Table 4-1 shows the combined results from the spectrometry for all irons, with final value averaged from four readings. Full data of all readings from the spectrometry can be seen in Appendix 4.

The samples for microstructural analysis were machined from the tensile bar blanks of the three irons while some blanks were machined into tensile test bars for the strength analysis. From the strength tests, three principal characteristic were established, Ultimate Tensile strength (Rm) or UTS which corresponds to the maximum stress attained during the tests. The yield stress ($Rp_{0.2}$) representing the plasticity threshold or elastic limit and failure strain (A_5%) which constitutes the plastic deformation of the samples through rupture. The microscopic analysis evaluates the matrix type and graphite properties of the irons. The graphite properties determine, three basic nodule attributes namely, the nodularity which in the context of SSFs, would mean graphites with more than 70% circularity or shape factor (S.f) greater than 0.7, the volume fraction of either ferrite or perlite and the nodule counts which describes the amount of graphite nodules per square area of the sample evaluated conforming to nodularity greater or equal to 70% and finally. The nodule counts and nodularity were evaluated on different criteria, the former in three categorization of shape factor (S.f) 0.7, 0.9 and perfectly spherical nodules at unity (1.0), while the latter was evaluated based on “area” and on “nodule count”. The “area” criterion describes percentage area of spherical nodules in the total nodule area of the analyzed sample while the nodularity by count expresses percentage spherical nodules based on nodule counts in the samples. Using these different criteria for nodularity and nodule counts opens up the possibility of many inferences depending on assessment perspectives or application.

4.1.1 Microstructural analysis

The as-cast samples for the microstructural analysis was sectioned from each of the three alloys and then prepared using standard metallographic techniques. The samples were first ground using Silicon carbide paper (SiC-paper) with surface grits from 80 to 1000 and polished with up to 1-micron paste smoothness to get the un-etched surface microstructures. Further treatment for etching using 2% Nital for the etched micrographs was then performed on the samples. The preliminary grinding and polishing activity was necessary to rid the samples of machining scratches or lathe marks for a more discernable micrograph before and after etching. Optical microscopy (using Nikon Epiphot 200) for the microstructural analysis was done for normal and 10X magnifications using similar methods employed in Dasgupta et al[53] and Hsu et al[17]. The matrix structure was determined through visual inspection against reference images while nodularity and graphite morphology were analyzed using guidelines from the ASTM standard A-247. All these micro-constituents were then further compared against specifications for SSF irons provided in EN: 1563 standard. The micrograph analysis were completed with a scientific image processing open-source software (ImageJ)[54] and as defined in the software’s specification, its characterization algorithms for nodule counts and nodularity ratings follows recommendations from the ASTM E2567-11 standard[55,56]. Figure 4.2 shows an overview of the process used in image analysis of the micrographs taken from the samples from this software.

Table 4-1: Combined Spectrometry analysis for the three irons

Iron 1	EN-GJS-600-10										
	C	Si	Mn	P	S	Cu	Al	Cr	Mo	Ni	
	%	%	%	%	%	%	%	%	%	%	
	2,77	4,356	0,289	0,019	0,0042	0,025	0,021	0,087	0,0056	0,112	
	2,746	4,442	0,287	0,018	0,003	0,023	0,019	0,084	0,0049	0,105	
	2,717	4,398	0,29	0,018	0,0029	0,023	0,019	0,085	0,0062	0,106	
	2,74	4,36	0,291	0,018	0,0035	0,023	0,019	0,085	0,0055	0,107	
Avg 1	**2,743**	**4,389**	**0,289**	**0,018**	**0,003**	**0,024**	**0,020**	**0,085**	**0,006**	**0,108**	

Iron 2	Co-2%										
	C	Si	Mn	P	S	Cu	Al	Cr	Mo	Ni	Co
	%	%	%	%	%	%	%	%	%	%	%
	2,7135	4,381	0,2915	0,0175	0,00285	0,0220	0,0180	0,084	0,0058	0,104	1,951
	2,7016	4,3778	0,2924	0,0172	0,00263	0,0214	0,0174	0,0835	0,0059	0,1026	1,91
	2,6897	4,3746	0,2933	0,0169	0,00241	0,0208	0,0168	0,083	0,006	0,1012	1,884
	2,6778	4,3714	0,2942	0,0166	0,00219	0,0202	0,0162	0,0825	0,0061	0,0998	1,866
Avg 2	**2,696**	**4,376**	**0,293**	**0,017**	**0,003**	**0,021**	**0,017**	**0,083**	**0,006**	**0,102**	**1,903**

Iron 3	Co-4%										
	C	Si	Mn	P	S	Cu	Al	Cr	Mo	Ni	Co
	%	%	%	%	%	%	%	%	%	%	%
	2,6659	4,3682	0,2951	0,0163	0,00197	0,0196	0,0156	0,082	0,0062	0,0984	4,114
	2,654	4,365	0,296	0,016	0,00175	0,019	0,015	0,0815	0,0063	0,097	4,035
	2,6421	4,3618	0,2969	0,0157	0,00153	0,0184	0,0144	0,081	0,0064	0,0956	3,98
	2,6302	4,3586	0,2978	0,0154	0,00131	0,0178	0,0138	0,0805	0,0065	0,0942	4,029
Avg 3	**2,648**	**4,363**	**0,296**	**0,016**	**0,002**	**0,019**	**0,015**	**0,081**	**0,006**	**0,096**	**4,040**

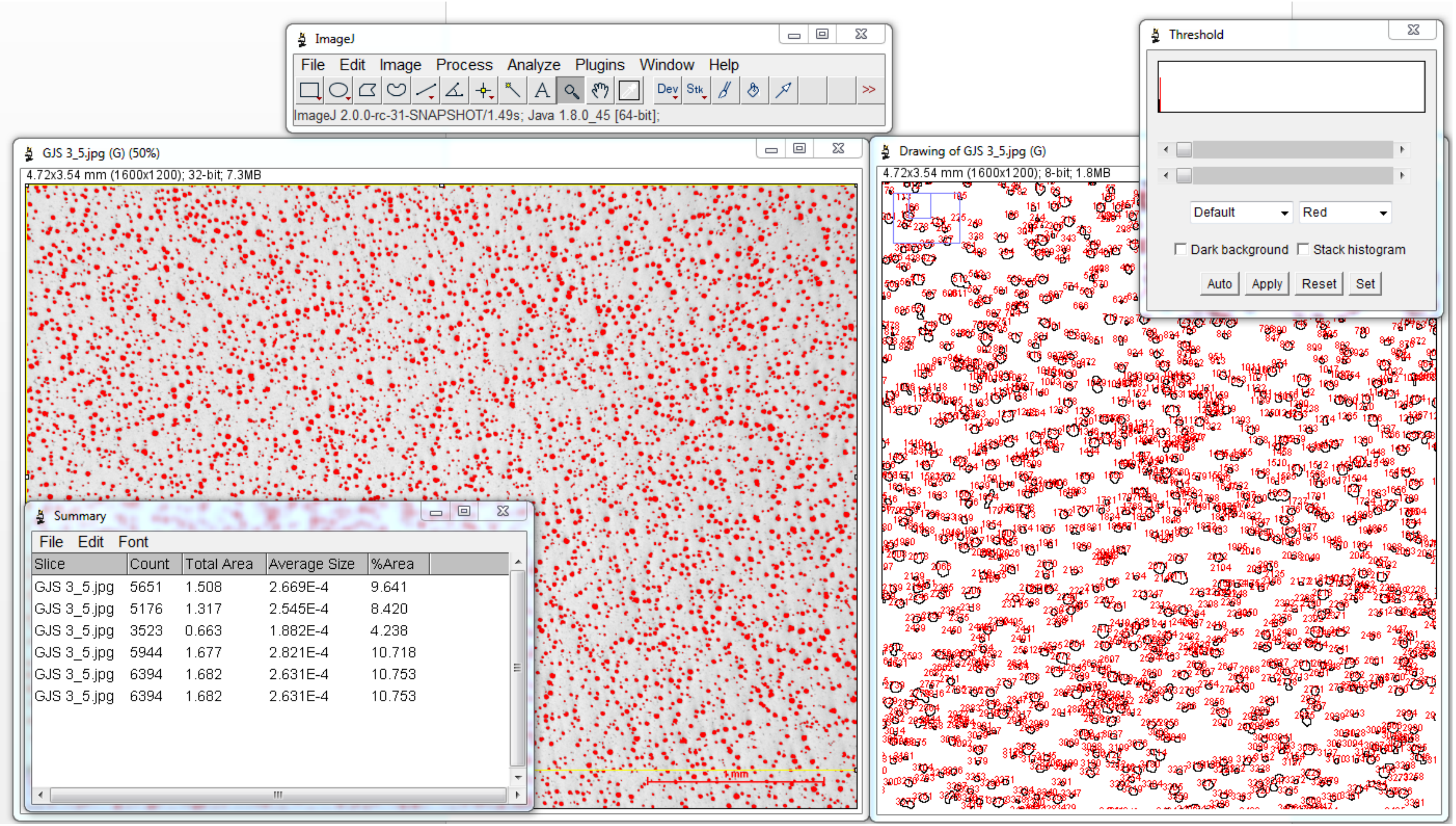
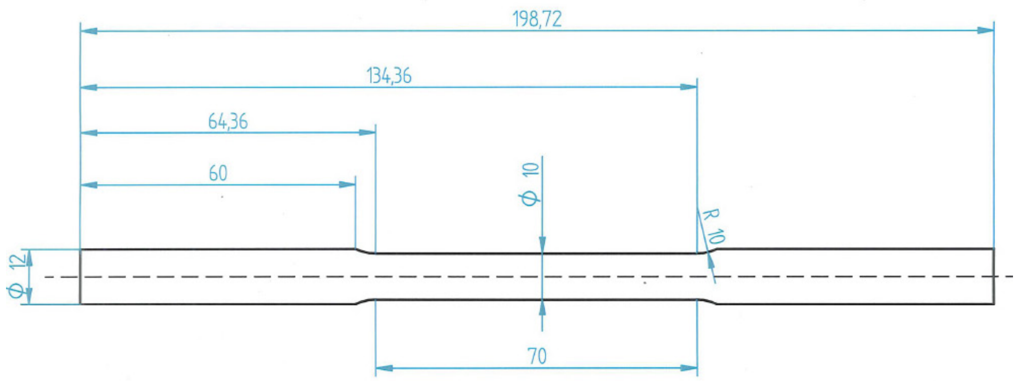


Figure 4-2: Overview of Image processing software used for micrograph analyses

4.1.2 Static mechanical analysis

Strength analysis for the three samples was performed with a 100kN servo-hydraulic dynamic testing system (MTS 810) shown in figure 4.4. Two sample specimens from each casting were machined and tested and an average of these values collated. The analysis procedure follows requirements from the ASTM standard E-8M[57] and the test specimens' dimensions are shown in figure 4.3. As seen from the figure, the parts of the bar at opposite ends with larger diameters (12mm) are placed in the wedge grip of the test machine while the mid-part with the original diameter (10mm) and gauge length (70mm) represents the core part of the test bar where actual measurements are taken. The change in gauge length and diameter of this middle part gives the elongation values at rupture and the ratio of the time-dependent applied loads and the geometric area of this part provides the tensile stress values. Further estimations of the Ultimate tensile strength (UTS) and yield strength were then estimated from the stress-strain curves from data output from the tests. Due to the scope of this thesis, the fracture surface of specimens were only visually inspected to observe fracture patterns at failure, lending some evidence to the material behavior in relation to composition or metallurgy when ruptured.



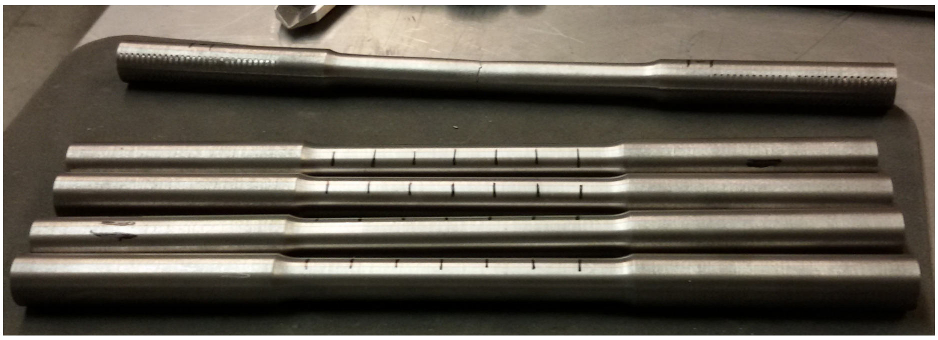


Figure 4-3: Tensile test Specimen dimensions (mm)

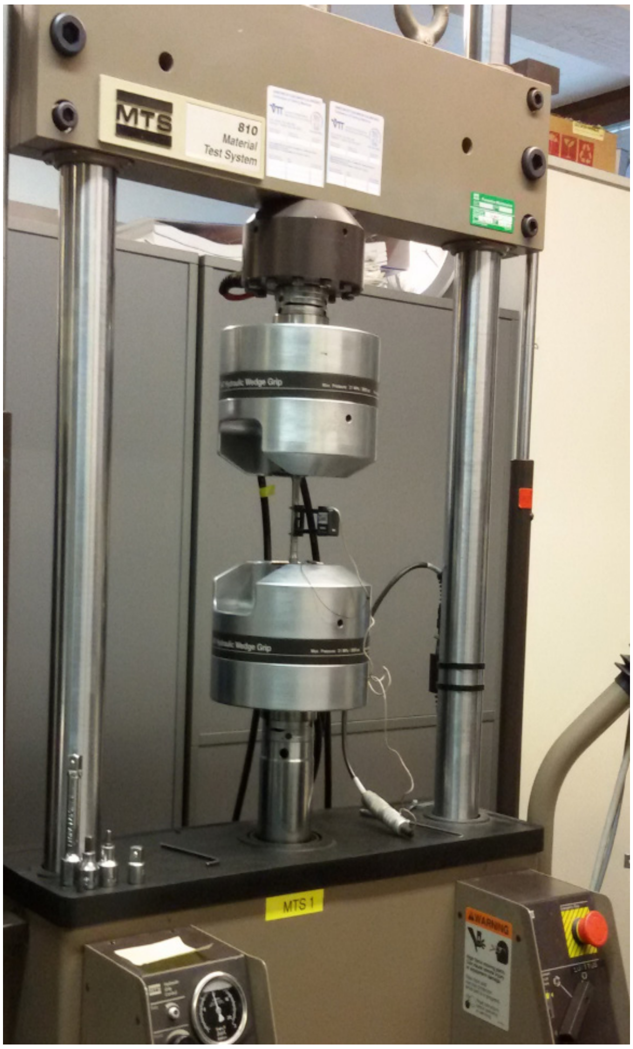


Figure 4-4: (a).Images of tensile test bars (b): Tensile testing machine (MTS 810)

Additionally, hardness measurements were done with a Brickers-220 (Gnehm) hardness tester at a test load 10kg for Vickers hardness. The average of three different readings on each sample, same used for the microstructural analysis were taken. The three points were chosen randomly on the samples since the micro-hardness analysis was not expressly essential for the scope of this thesis. All mechanical tests described in this section were implemented at room temperature and in the ambient atmosphere.

5 Results

5.1 Microstructure

The micrographs of the as-cast samples of GJS-600-10, 2% Co-SSF and 4% Co-SSF irons in both un-etched and etched conditions are shown in the figures 5-1 and 5.2. The un-etched microstructure indicates major micro-constituent properties of the iron including graphite shapes, size and distribution across the surface. The major difference with etched samples are clear distinguishable surface showing matrix type, grain boundaries, and graphite morphology specifically in the etched micrographs of 10X magnification. A summary of the microstructural properties from the metallographic analysis of the three samples is presented in Table 5.1.

Table 5-1: Microstructure properties of the SSF Iron and Co-alloyed Iron

Sample	Nodule count (Nodule/mm^2)	Avg nodule size µm^2	Nodularity %	Graphite %	Ferrite Matrix %	Perlite (projected) %
600-10	286	517	86	14.65	≥ 83.35	< 2
2% Co-iron	352	321	88	11.44	≥ 84.56	< 4
4% Co- Iron	392	296	88	11.52	≥ 84.48	< 4

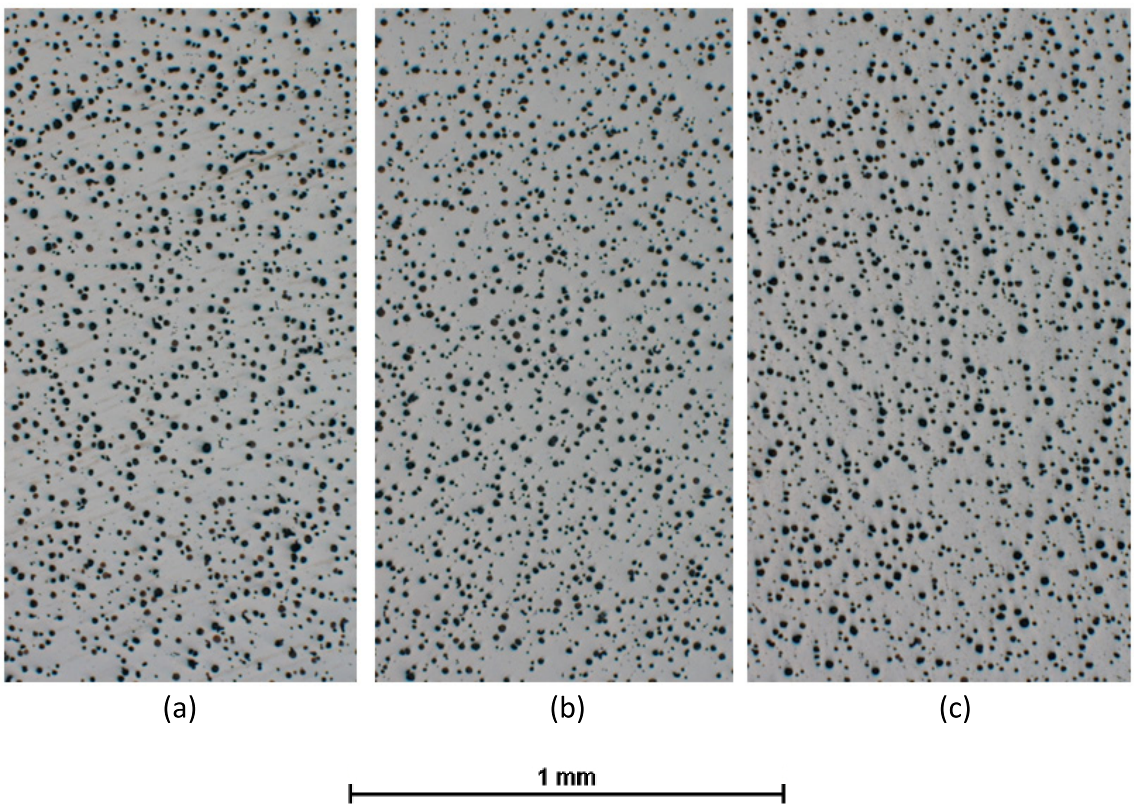


Figure 5-1(a): Un-etched microstructure of the (a) 600-10, (b) 2%-Co and (c)4%-Co Irons.

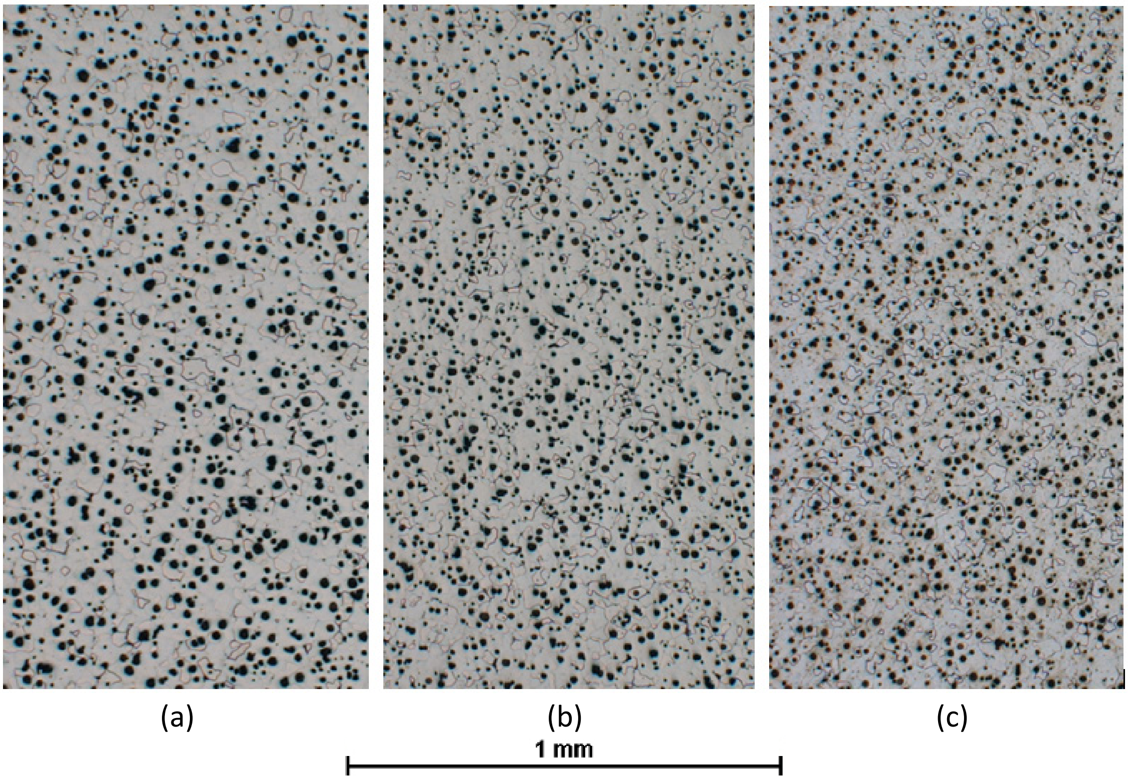


Figure 5-2: Etched microstructure of (a) EN-GJS-600-10, (b) 2%-Co and (c) 4%-Co Iron

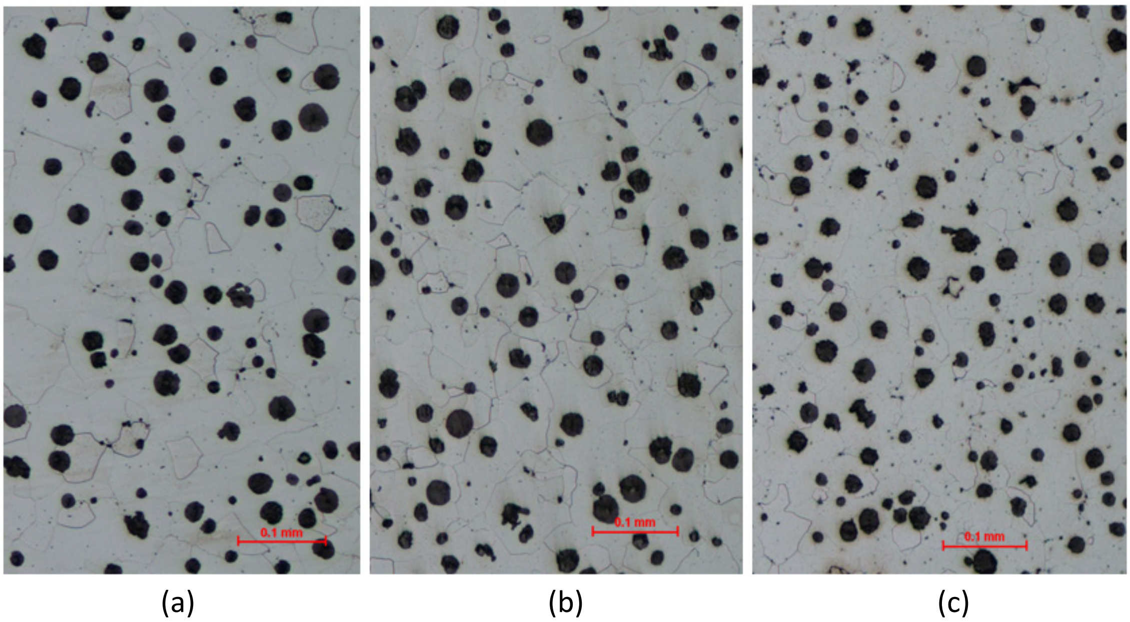


Figure 5-3: Etched microstructure of (a) EN-GJS-600-10, (b) 2%-Co and (c) 4%-Co Iron

In analysis of the graphite properties, all nodule sizes (in area) less than 25μm^2 were not considered for evaluation and thus excluded from the results. The shape factor (S.f) or "spheroidicity" of the nodule is also one of the criteria utilized in analysis. According to provisions from the ASTM E-2567 standard, nodules with shape factor greater than 0.6 are sufficient for DI characterization and within the scope of SSF iron, the categorization of graphite shapes V and VI preferred for this grades are firmly within similar shape factor range. Therefore the metallographic examination would only consider nodules with shape factor upward of 0.70. Apparently from the micrographs, all three sample from the castings have nodules adequately greater than 0.6 in shape factor and using the area-size criteria, nodule counts increased from 286 nodules/mm^2 in 600-10-SSF to 352 nodules/mm^2 and 392 nodules/mm^2 in the 2% and 4% Co-irons respectively as presented in Table 5.1. This represents about 38% increase in counts and verifies suggestions that Co alloying results in higher nodules amount in the study by Hsu et al[17].

Similar trend, although marginal was seen in nodularity (by count) at 88% for the Co-alloyed irons to 86% for the 600-10-SSF iron. While table 5.1 only introduces the highest nodularity value, analysis also revealed nodularity (by count) for nodules at S.f 0.9 and unity (1.0) at 73% and 38% for the 600-10-SSf compared to 77%, 45% and 80%, 52% for the 2% and 4% Co-alloyed iron respectively. These values point out that the spheroidicity of the nodules noticeably improve from the 600-10-SSF to the Co alloyed irons.

More so, the nodule sizes are appreciably smaller and refined in the Co-alloyed irons. This observation is corroborated by average nodule size values recorded from the micrograph analysis data for all three samples. The average nodule area decreased from 517µm^2 in the 600-10-SSF to 321µm^2 and 296µm^2 for the 2% and 4% Co alloyed irons.

In the case of matrix type, both etched and un-etched micrographs provides compelling evidence that all three irons have an almost entirely ferritic matrix as seen in Figures 5-1 to 5-3. Closer inspection of the Co-alloyed irons however showed very minute patches of perlites at some points in the microstructure. The volume fraction of perlite in both cases are regarded to be much less than the 5% allowable percentage stipulated in the EN: 1563 for SSF irons. The graphite percentage also decreased from the 600-10-SSF in comparison with the Co-alloyed irons effectively increasing the volume fraction of ferrite in the Co-alloyed irons. Figure 5-4 below summarizes the different parameters discussed above, comparing the microstructural characteristics of the experimental irons and 600-10-SSF.

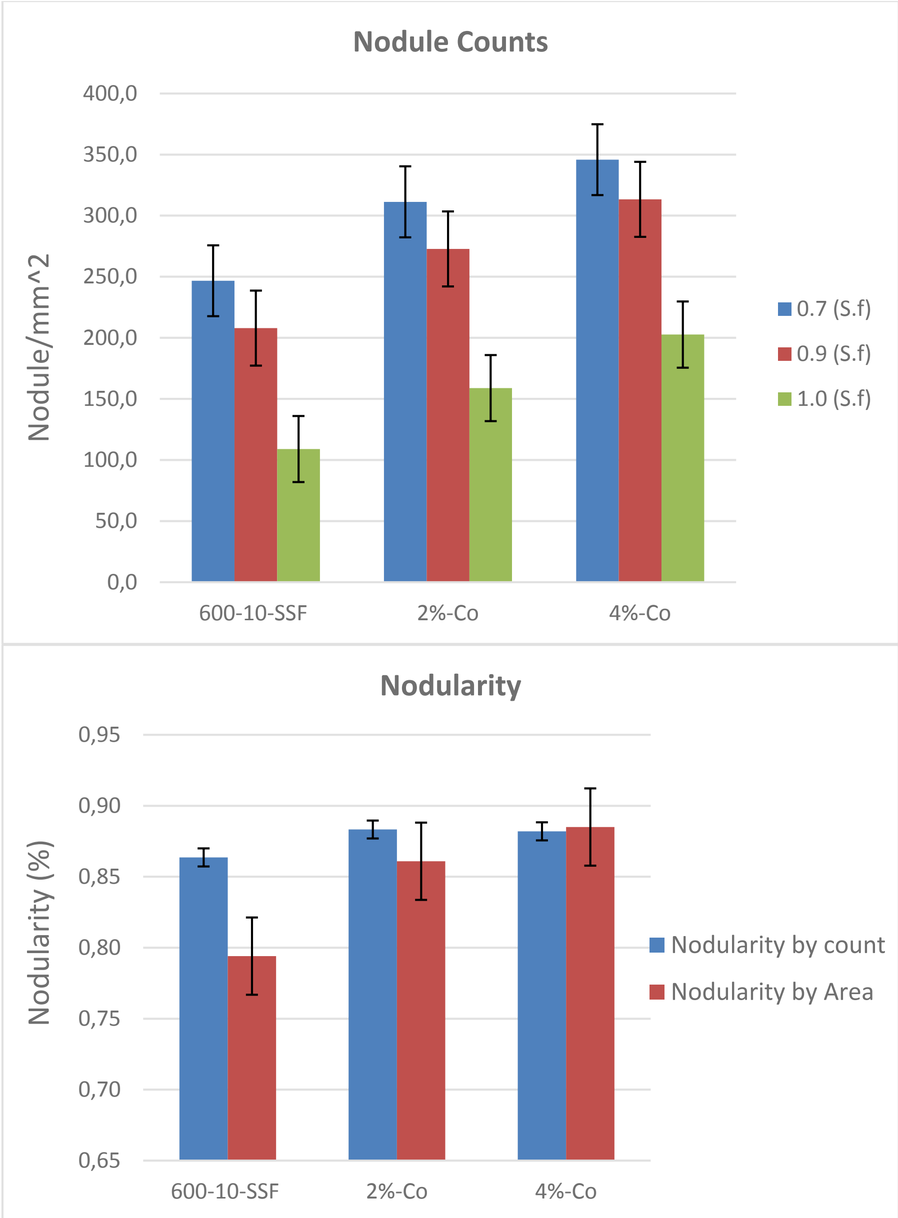


Figure 5-4: Comparison of graphite properties of the three irons (a) Nodule counts: S.f implies shape factor. (b) Nodularity

5.2 Mechanical properties

The results of mechanical tests on the three samples are summarized in the table 5-2, values averaged from results from two test specimens of each samples. The 4%-Co Iron had the highest yield and tensile strength at 525Nmm^{-2} and 686Nmm^{-2} than tensile values of 649Nmm^{-2} for the 2% Co iron and 612Nmm^{-2} for the 600-10-SSF. The increased strength in the Co-alloyed samples can be attributed to similar effect of solution strengthening of Co as with Si in the irons.

Also, the marginal increase in the matrix in the Co-alloyed iron coupled possibly with presence of perlite patches which otherwise were not seen in the 600-10-SSF contributed to the increase in strength.

Likewise, elongation values for the three samples returned a remarkable 19.5% elongation value for the experimental Co-alloyed SSF. The high elongation is evidently influenced by the combination of higher nodule counts, enhanced nodularity and refined graphite morphology. The amount of near spherical and perfectly spherical nodules in these irons are a huge leap from the 600-10-SSF and even conventional DI. The largely ferrite matrix also contributes to this. The increase in hardness obviously precursory to similar peaking in strength values. Significant increase were recorded in experimental Co-alloyed irons. Maximum value of 245 HV30 was registered for the 4%-Co iron versus 240 HV and 229 HV for the 2%-Co iron and 600-10-SS. As mentioned earlier, the hardness values for each iron were averaged from results from hardness readings from three random points taken from each sample.

Table 5-2: Summary of mechanical properties of the three Irons

Material Sample	Elongation A_5 %	Yield strength $Rp_{0,2}$ Nmm^{-2}	Tensile Strength Rm Nmm^{-2}	Hardness HV	Q** value
600-10 -SSF	17.8	498	612.16	229	6.67
2% Co -SSF	19,0	510	648,62	240	7.99
4% Co -SSF	19,5	525	685,70	245	9.17

**where $Q = (tensile\_strength^2 * elongation)$

In order to characterize the casting quality of the three tested samples, the Q-value introduced in a statistical study by Siefer, 1970 to describe the relationship between tensile strength and elongation was also calculated. As enumerated in table 5-2, the Q value for the experimental Co-alloyed irons showed that the qualities of these irons are better than the standardized 600-10 SSF. This was quite visible even before the computation of Q-value considering these irons returned higher tensile strength and elongation.

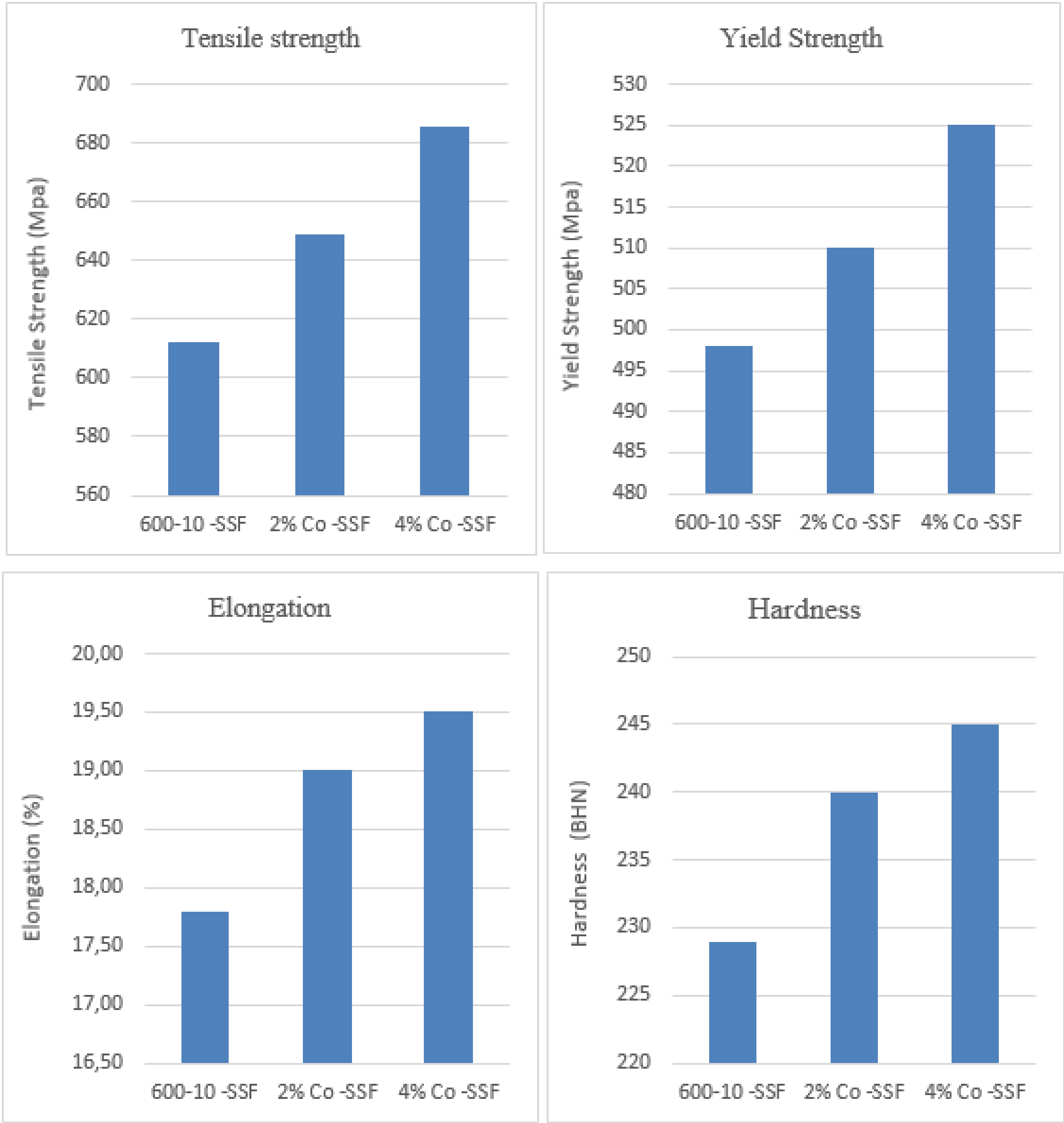


Figure 5-5: Mechanical properties for the 600-10 Vs Co-alloyed irons

6 Discussion of Results

6.1 Graphite properties

Improvement in graphite properties and strength recorded for the experimental Co-alloyed irons summed up the most significant effect of Co in the chemical composition. The graphite properties provides an explanation for the elongation results and casting quality. As expected, results from the optical microscopy analysis from all three irons, the GJS-600-10 and Co-alloyed experimental SSFs shows a dominant ferrite matrix with no obvious signs of graphite degeneracy thus confirms similarity in both Si and Co as strong ferrite promoters. The perlite content in the matrix is estimated to be less than the allowable 5% of total micro constituent in the iron as specified in the EN 1563 for SSF irons. Despite the known effect of Si as a strong graphitizer and ferrite promoter, similar stronger action for Co is quite apparent from the microstructural results showing increased nodule counts, smaller graphite size and refined spherical nodules in agreement with conclusions from studies into Co-alloying in DI by Hsu et al, 2007 and Modl, 1972[58].

1. The higher nodule count, improved morphology and enhanced nodularity accounts for the better elongation seen in the experimental Co-alloyed irons compared to the standardized 600-10-SSF. The gains in nodule counts and nodularity in the experimental irons can be credited to the austenite stabilizing effect of Co in the irons. This property enables better carbon diffusion in an increased nucleation sites for eutectic graphites in the microstructure. In current SSF grades, the high Si have been linked to influence aggregation of CHG due to large formation of heterogeneous nucleation sites and drop in melting point of austenitic shells. The stability provided by the addition of Co in the iron improves impending lattice de-registry with austenite found in oxidized iron containing numerous Si oxide particles. Therefore, the better nodularity in the Co-alloyed irons minimized notch effects from the nodules thereby increasing strength needed to propagate dislocation movement.

2. The microstructural assessment also revealed improved and refined graphite morphology in the experimental Co irons. The average nodule size decreased from 517μm^2 for the reference 600-10 to 321μm^2 and 296μm^2 for the 2% and 4% Co-alloyed experimental SSF respectively. Such because nodularisation

efficiency is higher in the Co-alloyed irons arising from a shift in levels of heterogeneous nucleation sites also due to stabilized austenite. The choice of inoculants containing Ca, Ba along with ferrosilicon also played a vital role in microstructural properties. Inoculants present and solidification condition determine the nucleation temperature and the eutectic cell counts. They also influence the solidification condition when growth starts

3. Although, microstructural evaluation did include a fractograph analysis to examine failure pattern of the irons or dispersive extent of Co or other alloying element in the composition. Visual inspection of the fractured samples and speculative inferences from using similar base composition for all three irons suggests that potential segregation from chill carbides, Si or Co is kept to a very minimum in these castings. The 600-10 iron casting meeting its mechanical properties requirements as designated in the standard also supports this conjecture. Nevertheless, it is noteworthy that detailed fracture analysis is necessary to definitively validate this conclusion.

6.2 Mechanical properties

The mechanical properties of the three irons samples are consistent with the composition and microstructure of the irons. While ferritization by Si is well documented and expected for the 600-10 iron, similar results for the Co alloyed irons shows that Co also promotes ferrite. Co influences the diffusion of carbon through the ferrite shell, moving the knee of a transformation diagram to lower time interval stabilizing the ferrite matrix and resulting in reduced perlite formation.

4. From the results of the Co-alloyed irons, the better UTS and yield strength can be explained through the solution strengthening effect of Co on the matrix. While exact volume fraction of ferrite in the microstructure cannot be precisely quantified with metallographic analysis tool used, hardness increase corresponds to the improvements seen in strength for the Co-alloyed irons indicating matrix homogeneity. Co in addition to improving nodule formation[5,17] also influence more ferrite formation through its austenite stabilization capabilities within eutectic graphites cells. While Silicon possess similar influences on the iron, the difference between both is the sensitivity of Si to forming CHG above certain amount in the composition if improperly managed.

5. It was also found that the finer and homogenous microstructure was influenced by the increased nodule counts which provided more nucleation sites for ferrite growth and reduction of segregation potential for deleterious elements in the melt[59] which are often responsible for the presence of intercellular carbides, pearlite and degenerate graphite.

Owing to a refined matrix, eutectic cell carbides, perlite or degenerated graphites cannot be precipitated making dislocation movement difficult to propagate. These different factors relating to the matrix however possess different effects on mechanical properties.

6. Nodule count influences the pearlite content in as-cast DI. Increasing the nodule count decreases pearlite which then affects strength and increases elongation. Improved nodule counts, through the reduction of chill carbides, segregation carbides, and carbides associated with "inverse chill", improves ductility and from a production point, machinability of the casting.

7. The increased nodule counts in the Co-alloyed irons and efficient nodularisation again owing to austenite stability by Co alloying influenced graphite size and shape. Using deductive inferences relating this outcome to results from similar studies in Co-alloying, fatigue and fracture properties in the experimental Co irons are expected to be improved.

8. The overall quality measured with the Q-value indicate that increased nodule counts is an important feature and highlight of the experimental Co irons in this thesis work. As shown in figure 6-1, the effect of the hiked counts in the Co-alloyed irons contributed to both elongation and strength of the iron which is evident on overall casting quality.

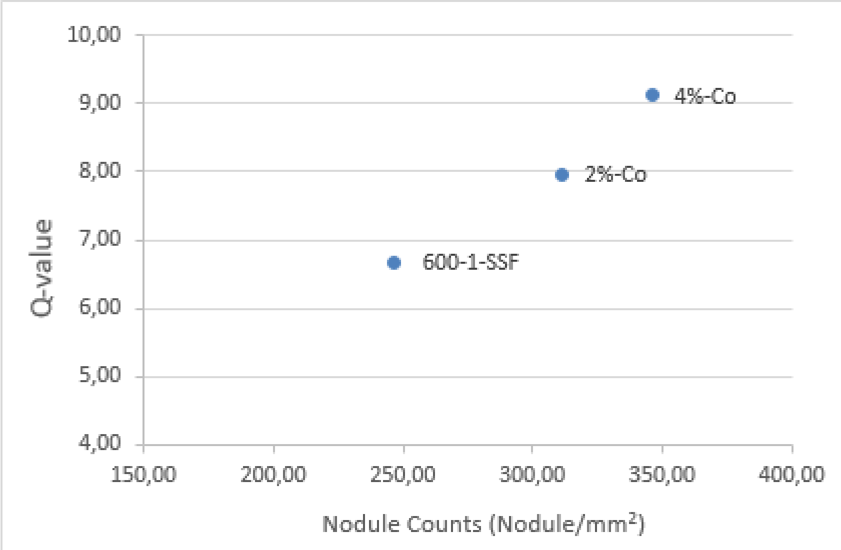


Figure 6-1: Effect of nodule counts on overall quality of the Irons

From the points raised in the section above, it can be argued that hardness as well as strength are as much dependent on the matrix as they are on graphite properties.

The nodule count, graphite morphology and matrix in the Co-alloyed irons are consistent with results of studies on Co alloying in DI from Hsu et al, 2007, Modl, 1972 and Appleton (as cited in Shen, 1995). Similar conclusions based on graphite characteristics reported in these studies can be inferred that the Co-alloyed irons compared to the 600-10-SSF would also offer better toughness properties. Toughness typically represents a good balance between strength and ductility which are better in Co-alloyed irons. Same inference on impact energy, cannot however be ascertained from the mechanical analysis results due to its dependence on temperature.

Nonetheless, the amount of Co alloyed with DI for significant effect is also one factor to be considered when considering strengthening with Co. A general overview of studies, both within cast iron and steel production have typically used quite high alloying percentages of Co. Comparing studies with varying amounts of Co for instance Hsu et al, 2007 (4% Co), Shen et al 1995 (0.5% Co), and Modl, 1972, (1% - 15% Co), indicated that relatively large Co alloying provided better results on microstructural and mechanical properties with corresponding increase in graphite properties and strength.

Overall consideration of all three irons in this thesis work, suggests that similarities in influence and behavior of both Si and Co are characteristically similar making it difficult to expressly quantify individual effect of either alloying element on properties of the cast irons. This in effect raises the question of whether Co and Si counteracts or each other to have any significant effect. Especially in the 4% Co irons with an approximately equal amount of Si in the irons. It can of course be suggested that increasing Co can produce further strength increase and elongation for the irons going by a linear forecast of the data points from the strength testing. However, data points from the three irons tested in this thesis work, are statistically insufficient to project on what form or type of increment will be derived for irons with increasing amounts of Co.

Within the body of studies relating to strengthening SSF irons, this thesis work is the first of such research endeavors, the result of which cannot be conclusively related to all grades within the SSF family. There is not enough evidence from this work alone to prove either the EN-GJS-500-14 or 450-18 would behave similarly. In similar perspective, although there is considerable difference in mechanical properties between the 2% and 4% Co-alloyed 600-10, it is still a bit difficult to clearly claim or understand if the strength increase for instance between these two irons will either be continuously proportional to Co percentage increase or plateau out as some alloying quantity. It might also be the case that a 2% difference in alloying content is not sufficient enough to visualize this. Hence the need for a more detailed work utilizing differing amount of Co.

Additionally, knowledge of Co alloying especially in DI casting is generally lacking which and as such, considerable independent assessment of its properties in combination with traditional DI composition should be adequately understood before reincorporation into SSF use.

6.3 Recommendation for further studies

Generally, while the results derived from tests satisfies the intended objectives of the thesis work, there are still important questions relating to the use of cobalt alloying that remained unanswered. And also some due to inconclusive evidence based on the extent of the implemented tests within the scope of this work.

Although, there appears to be remarkable difference in properties between the 600-10 SSF and Co-alloyed iron, further exploratory study of Co in SSFs with Si level above the identified critical percentage of 4.3wt% would be a good insight and stronger validation of the effect of Co-alloying in creating higher strength SSF. With results from such studies, the exact role of Co in actual quantifiable measures in this regard can be adequately verified. More so, the issue of CHG is still not ideally addressed within the context of the results and casting trials. Further casting trials with heavier casting sections traditionally prone to CHG should be implemented to examine the effect of Co. Definitive assessment and tests on toughness, impact strength and fracture analysis would be a useful supplement to the tests reported here in the report. It gives more credence and fuller characterization to the properties of the experimental alloys. In addition, SEM analysis and the material behavior at elevated temperatures would also be application to the attribute portfolio of the Co-alloyed irons.

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7 Appendices

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7.1 Appendix 1. Scrap composition and melt charge.

Panoslaskenta

Tiedot:

Yleiset:

Valu Päivämäärä :	18.2.2014	Valu:							tähtäys loppusulaan
Uuni :	Taylor	**Sulaa Uunissa:**	312,5 kg						
Materiaali :		**Sulan Lop. Paino:**	317,8 kg						
Kok. Tuotepaino:	0,0 kg	**Senkka #1:**	105,0 kg		Cu	0,63 kg	0,3 %	210 I	0,30 %
Kok. Valupaino:	0,0 kg	**Senkka #2:**	105,0 kg	lisäys uuniin ensimmäisen kaa	Co	4,2 kg	2%	210 kg	2 %
Sulatettava Määrä:	300,0 kg	**Senkka #3:**	105,0 kg	lisäys uuniin toisen kaadon jälk	Co	2,1 kg	2%	105 kg	4 %

Standardit:

	C	Si	Mg	Mn	P	S	Cu	Cr	Co	Nb	Ni
Kaisu	2,88	4,3	0,04	0,3							
HS1	2,88	4,3	0,04	0,3			0,3		2		
HS2	2,88	4,3	0,04	0,3			0,3		4		
									6		

Panoslaskenta:

laskennallinen massa [kg]

Panos Uuniin:	[kg]	C	Si	Mg	Mn	P	S	Cu	Cr	Al	Sn
kiertoromu GJL-250	0,0 kg	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Särkinen paksu	90,0 kg	0,08	0,32	0,00	0,90	0,01	0,00	0,00	0,00	0,03	0,01
harkko Peiron	210,0 kg	8,61	2,24	0,00	0,03	0,04	0,01	0,00	0,00	0,00	0,00
silppu Lokomo	0,0 kg	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
FeSi	11,5 kg	0,01	8,63	0,00	0,00	0,01	0,00	0,00	0,05	0,23	0,00
FeMn A	0,0 kg	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
C	0,95 kg	0,76	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Senkkaan:											
Senkka #1:											
Cu	0,00 kg	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
FeSiMg	1,10 kg	0,00	0,51	0,06	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Ultraseed	0,67 kg	0,00	0,50	0,00	0,00	0,00	0,00	0,00	0,00	0,01	0,00
Senkka #2:	Käytä vain jos erilaiset koostumukset senkkoihin										
Cu	0,00 kg	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
FeSiMg	0,00 kg	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Ultraseed	0,00 kg	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00

Analyysi:

Esi-näyte Tavoite:

C	Si	Mg	Mn	P	S	Cu	Cr	Al	Sn
3,028	3,577	0,000	0,296	0,017	0,004	0,000	0,015	0,082	0,003

Valu-näyte Tavoite:

C	Si	Mg	Mn	P	S	Cu	Cr	Al	Sn	Si saanto
2,98	4,18	0,02	0,29	0,02	0,00	0,00	0,02	0,09	0,00	0,7
	4,28									0,8
	4,37									0,9

HUOMIOI Mn -pitoisuus uuninäytteestä. Saattaa vaatia täsmennystä.

7.2 Appendix 2. Inoculant Specification - FoundriSil

FOUNDRISIL® 75 INOCULANT

- More potent than conventional Cabearing inoculants in grey and ductile irons
- More cost effective than other Cabearing inoculants
- Optimum Ca and Ba contents minimises dross
- Can be used in both grey and ductile irons
- Especially effective in grey irons of lower sulphur content
- Fading resistant inoculant

Foundrisil® 75 inoculant is a 75% Si based alloy containing optimised amounts of calcium and barium to give very effective control of chill in grey and ductile irons. It is particularly useful in grey iron of lower sulphur content where many inoculants be come less effective.

Foundrisil® 75 inoculant was deve loped by Elkem on recognising the need for an economic inoculant that would be more effective than conven tional Cabearing ferrosilicon and which would retain its effect in grey iron of lower sulphur content. Exten sive laboratory tests led to the finding that balanced, relatively low levels of calcium and barium in ferrosilicon give more effective inoculation at moderate cost than conventional Cabearing ferrosilicon. The tests also show that the inoculant is effective down to lower levels of sulphur in grey iron than many other inoculants.

Foundrisil® 75 inoculant is produced to the following specification:

Chemical Specification

Silicon	72 – 78%
CalciUm	0.75 – 1.25%
BariUm	0.75 – 1.25%
AlUminiUm	0.75 – 1.25%
Iron	Balance

Production of Foundrisil® 75 Inoculant

Foundrisil® 75 noculant is produced at the Elkem Bremanger plant in Norway and the Elkem Chicoutimi plant in Canada, using special production methods to ensure maximum uniformity of composition and structure through out the product. Both Elkem plants have ISO 9001 and ISO 14001 accredi tations, in addition to ISO/TS 16949 certificate for Elkem Bremanger.

Ferrosilicon alloys containing elements such as calcium and barium have com plex structures consisting of a number of intermetallic com pounds. The solidification temperatures of these compounds vary and this can lead to extensive segregation if the alloy is allowed to cool slowly during casting. Because some of these com pounds are more brittle and crush more readily, this can lead to wide variations in the compositions of different particle sizes after crushing and grading.
At the Elkem Bremanger and Chicoutimi plants, Foundrisil® 75 inoculant is cast into thin slabs in iron moulds. This produces a very fine structure and avoids any risk of segre gation occurring during solidification. The composition of Foundrisil® 75 inoculant is therefore consistent over the entire range of particle sizes.

Application of Foundrisil® 75 Inoculant

Elkem supply Foundrisil® 75 inoculant grades suitable for both metal stream (MSI) and ladle inoculation upon customer request, each grade with a complete certificate of analysis.

Foundrisil® 75 inoculant should be added to the tapping stream as the ladles are filled or, preferably, as the metal is transferred from a transfer ladle to casting ladles. It is advised against to add the alloy to an empty ladle where it can oxidise or start to dissolve in any residual iron and thus lose its effect.

The effects of all inoculants start to fade immediately the addition has been made and it is advisable therefore to add Foundrisil® 75 inoculant as late as possible before pouring the moulds. However, the presence of barium in Foundrisil® 75 inoculant tends to reduce the fading rate thus giving more latitude to the time between inoculation and pouring.

Addition rates of 0.2 – 0.3%, or even less, are generally sufficient to give adequate chill control in grey iron of normal sulphur content. Slightly larger additions may be needed in grey iron containing below 0.05% S. Grey iron with less than about 0.025% S are notoriously difficult to inoculate and it is generally advisable to raise the sulphur content of the iron under these circumstances. The addition rates to ductile iron vary according to the grade of iron and the section thickness of the castings, but it is rarely necessary to add more than 0.5% Foundrisil® 75 inoculant to obtain the required effect.

Foundrisil® 75 inoculant is one of the most efficient and consistent economic inoculants for grey and ductile irons and its correct use should solve most inoculation problems whilst often giving some economic advantages.

Physical Data

Apparent Density	3.1 g/cm³
Bulk Density	1.75 g/cm³
Melting Range	1325 °C (liquidus)
	1208 °C (solidus)

Standard Sizes

In-stream/MSI	0.2 – 0.7 mm
Small Ladle	0.7 – 2 mm
Larger Ladle	2 – 6 mm

Standard Packing

Big Bag	1050 kg on pallet
Big Bag	1500 kg on pallet
Big Bag	500 kg on pallet
Paper Bag	25 kg on pallet
Steel Drum	200 and 220 kg

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7.3 Appendix 3. Nodulariser specification - Lamet

Elkem

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Product Data Sheet
Magnesium Ferrosilicon Nodularisers

1. Alloy Description
Magnesium Ferrosilicon (MgFeSi) is a high quality nodulariser with carefully chosen calcium and aluminium contents within the beneficial range for ductile iron production. Calcium helps control the magnesium reactivity during treatment and low aluminium minimises pinhole problems with green-sand moulds.

2. Effect in Iron
MgFeSi is the preferred alloy for nodularising ductile iron. For base iron free from harmful impurities, MgFeSi without cerium may be used. However, without the nucleating effect of cerium, chill may form in thin sections. Cerium and other rare earths effectively neutralise the harmful effects from subversive elements which may cause structural defects.

3. Application
MgFeSi is produced in a variety of grades, some of which are listed. This allows each foundry the flexibility to select the alloy best suited for their treatment method and other needs.

4. Chemical analysis
Elkem offers MgFeSi qualities in a variety of standard chemistries, some of which are shown in the table. Elkem can furthermore offer special qualities on demand. Please contact your local Elkem sales representative with any questions in this regard.

5. Sizes
Available in sizes suitable for all foundry methods including ladle, in-the-mould, and flow through processes.

6. Packing
The product is available in various forms of packing on request.

7. Physical Data

Apparent density	4.6 g/cm^3
Bulk density	2250 kg/m^3
Melting range	1225 °C(liquidus)
	910 °C (solidus)

Solubility:
Water : Insoluble
Mineral acids : Soluble, releases hydrogen

May form phosphine and arsine gas in contact with water, acids or bases.

Nodulariser	%Si	%Mg	%La	%Ca	%RE*	%Al	%MgO
Remag® 3100	44 – 48	2.75 – 3.5	–	0.2 – 0.5	1.75 – 2.5	0.4 – 1.0	–
Elmag® 5800		5.5 – 6.2	–	0.8 – 1.2	0.8 – 1.2	0.4 – 1.0	–
Lamet™		5.0 – 6.0	0.25 – 0.4	0.4 – 0.6	–	0.8 – 1.2	Max 0.45

*RE (Rare Earths) contains approximately 50% Ce, 25% La, 15% Nd, 5% Pr, minor amounts of Y and Sm.

7.4 Appendix 4. Spectrometry analysis

09-4-15 09:07:11

Valimoinstituutti

Sample Identification

Quality SampleNo esi500 2.4.2014

	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Al
	%	%	%	%	%	%	%	%	%	%
1.	2.770	4.356	0.289	0.019	0.0042	0.087	0.0056	0.112	0.025	0.021
2.	2.746	4.442	0.287	0.018	0.0030	0.084	0.0049	0.105	0.023	0.019
3.	2.717	4.398	0.290	0.018	0.0029	0.085	0.0062	0.106	0.023	0.019
4.	2.740	4.360	0.291	0.018	0.0035	0.085	0.0055	0.107	0.023	0.019
⇑										
↑										
Ø	**2.743**	**4.389**	**0.289**	**0.018**	**0.0034**	**0.085**	**0.0055**	**0.108**	**0.024**	**0.020**
↓										
⇓										
σ	0.022	0.040	0.0017	0.00058	0.00059	0.0013	0.00054	0.0032	0.0012	0.0012
υ	0.802	0.911	0.588	3.222	17.35	1.529	9.818	2.963	5.000	6.000

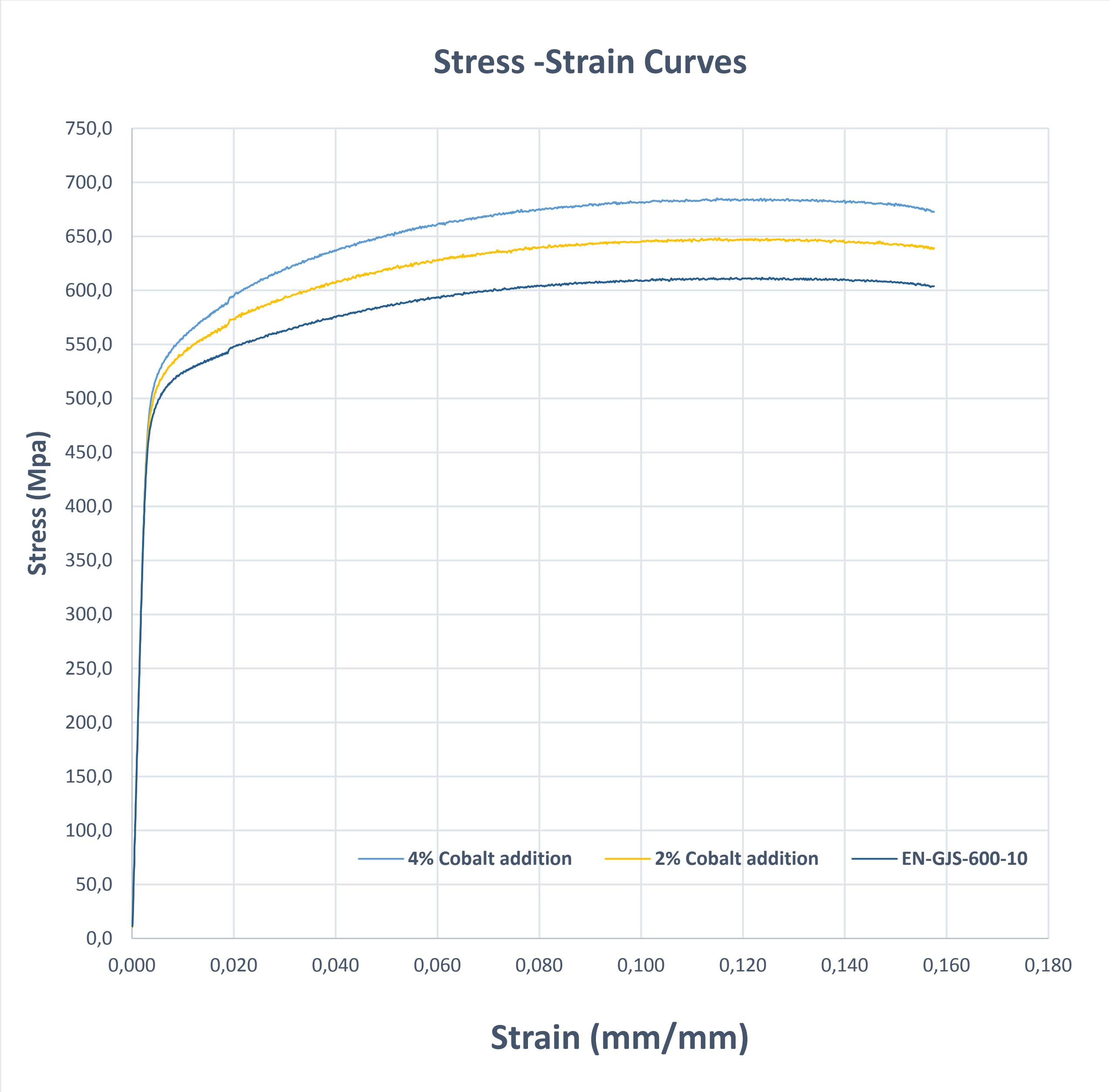
	As	B	Bi	Ce	Co	Mg	Nb	Pb	Sb	Sn
	%	%	%	%	%	%	%	%	%	%
1.	<0.0010	<0.00020	0.012	0.018	0.025	0.038	0.015	0.014	<0.0050	0.0066
2.	<0.0010	<0.00020	0.012	0.016	0.024	0.029	0.014	0.0074	<0.0050	0.0061
3.	<0.0010	<0.00020	0.016	0.020	0.025	0.028	0.014	0.011	<0.0050	0.0062
4.	<0.0010	<0.00020	0.015	0.019	0.024	0.027	0.014	0.0090	<0.0050	0.0062
⇑										
↑										
Ø	**<0.0010**	**<0.00020**	**0.014**	**0.018**	**0.025**	**0.030**	**0.014**	**0.010**	**<0.0050**	**0.0063**
↓										
⇓										
σ			0.0021	0.0017	0.00082	0.0051	0.00058	0.0029		0.00022
υ			15.00	9.444	3.280	17.00	4.143	29.00		3.492

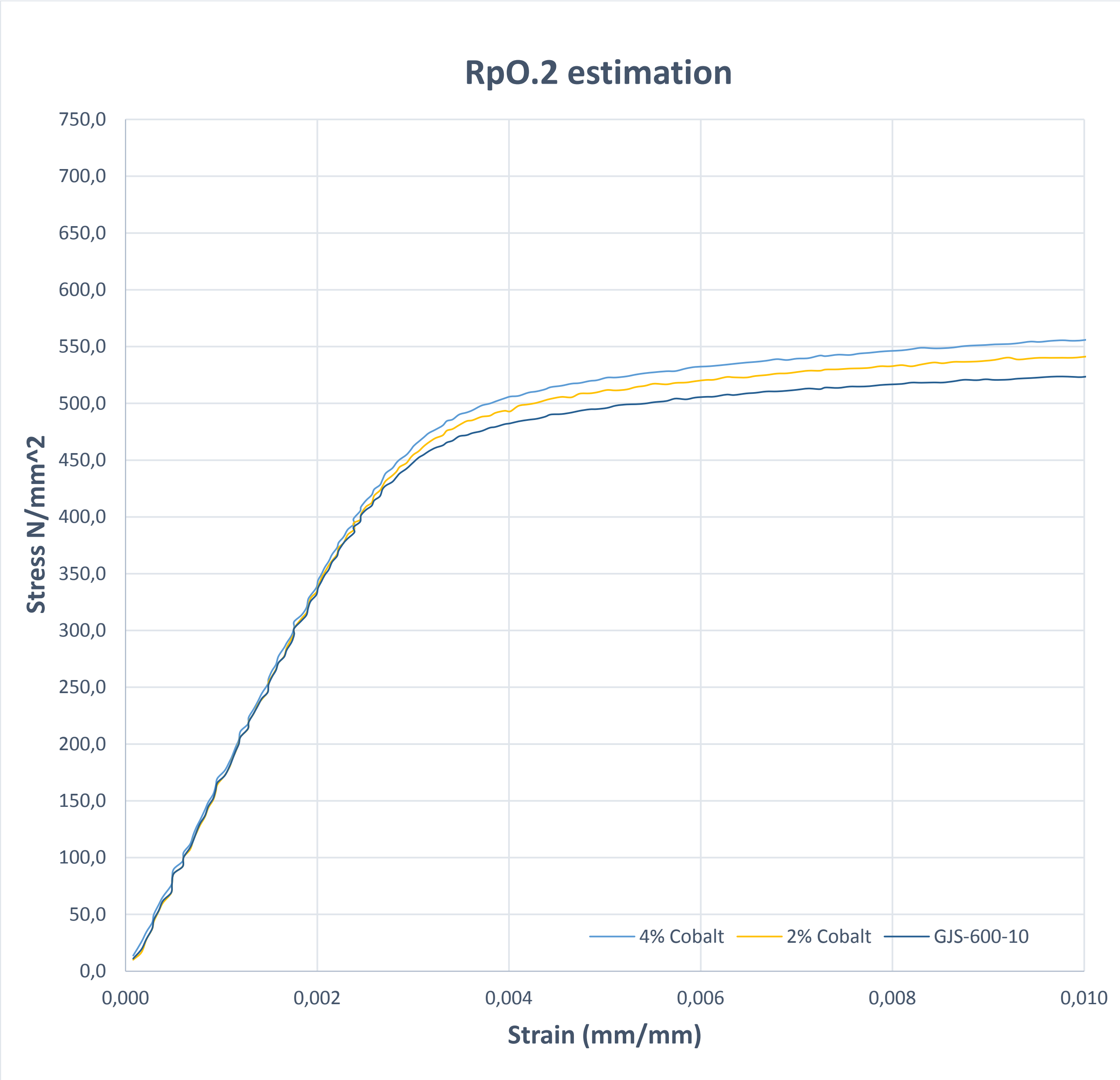
	La	Ti	V	W	Zn	Zr	Se	Fe	Ceq	
	%	%	%	%	%	%	%	%	[I]	
1.	0.0095	0.016	0.025	0.013	0.0025	0.0043	<0.0030	92.10	<0.0	
2.	0.0092	0.016	0.024	0.011	0.0023	0.0040	<0.0030	92.08	<0.0	
3.	0.0094	0.016	0.024	0.0072	0.0025	0.0041	<0.0030	92.14	<0.0	
4.	0.0096	0.016	0.025	0.0095	0.0021	0.0043	<0.0030	92.16	<0.0	
⇑										
↑										
Ø	**0.0094**	**0.016**	**0.025**	**0.010**	**0.0024**	**0.0042**	**<0.0030**	**92.12**	**0.0**	

Fe120 Concentrations
Bruker Elemental 1/2

↓								
⇓								
σ	0.00017		0.00082	0.0025	0.00020	0.00015		0.037
υ	1.809		3.280	25.00	8.333	3.571		0.040

7.5 Appendix 5. Stress- strain curves





RpO.2 estimation
750,0
700,0
650,0
600,0
550,0
500,0
450,0
400,0
350,0
300,0
250,0
200,0
150,0
100,0
50,0
0,0
Stress N/mm^2
0,000
0,002
0,004
0,006
0,008
0,010
Strain (mm/mm)
4% Cobalt
2% Cobalt
GJS-600-10